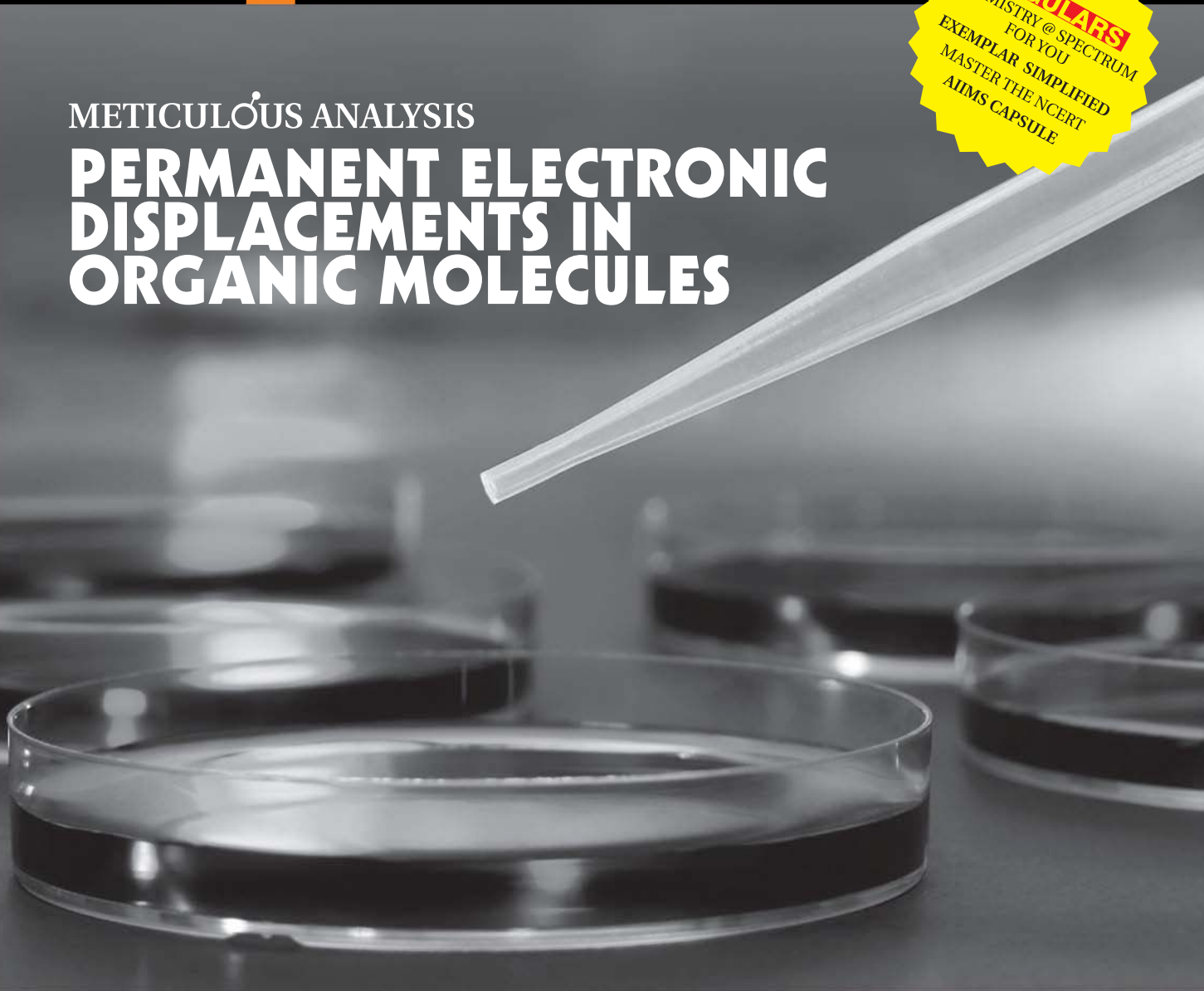


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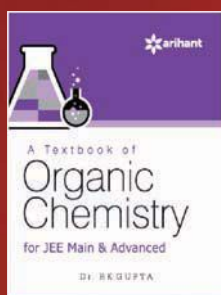


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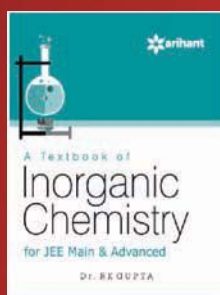
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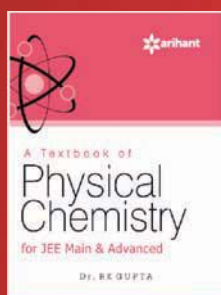
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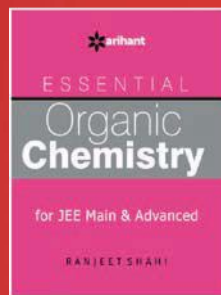
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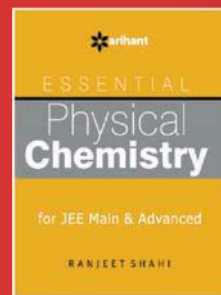
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Publisher PARUL JAIN
Chairman YC JAIN

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Cover & Layout Design SHANU MANSOORI
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Type Setting MAYANK, SANDEEP, ARJUN

Copy Editors SHIKHA
Proof Reader SWATI

Head Office ARIHANT MEDIA PROMOTERS
KALINDI, TP NAGAR, MEERUT-2

Phone 0121-2401479, 2512970

Fax 0121-2401648

E-mail spectrum@arihantbooks.com

Website www.arihantbooks.com

Circulation Regd. Office ARIHANT MEDIA PROMOTERS
4577/15, AGARWAL ROAD,

DARYA GANJ, NEW DELHI-2

PH. : 011-47630600

© Publisher

Printed and Published by Parul Jain for

Arihant Media Promoters

Printed at Arihant Publications (India) Ltd

T.P. Nagar, Meerut (U.P.)

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"AT THE END OF THE DAY, THE MOST OVERWHELMING KEY TO A CHILD'S SUCCESS IS THE POSITIVE INVOLVEMENT OF PARENTS."

JANE D. HULL



THE FINEST GUIDE

The role of Parents is very important in a child's education, especially for an IIT aspirant. IIT JEE is the test of both Intelligence and emotional quotient. That's why I consider, parental guidance as important as a mentor's role in sharpening your skills.

Parents play a very important role in the lives of their children. They have to build a solid foundation for their kids in order to provide them a successful and rewarding life. The foundation of an individual can be broken down into several different parts, such as morals, religious beliefs, political standpoints, and education, to name a few. Likewise a child

may also learn from many different sources e.g., from teachers at school, from TV programs, from their parents at home etc.

It is said that children learn the first and the most from their parents. I agree with this belief. Children spend most of their time with their parents and they are always watching what they did and how they did it. In most of the cases the first idols of a child's life are their parents. Even though they don't realize this.

There is another belief that people when became old are going to be just as their parents were. I can see this in my father, who is gradually adapting to my grandfather every day. Even he has started following those things from his father which bothered him earlier. These beliefs clearly indicate the importance of parents in someone's life.

The moral support that a parent can provide on your failures can't be expected from anybody else. However, sometimes it also

FROM THE EDITOR'S DESK

happens that parental support often turns out to be an added pressure. We can define this pressure as “**the pressure of expectation**” or the “**pressure of faith**” in you. This faith may inculcate a fear i.e., the fear of not standing up to their expectations or the fear of failure on the D-day. At such a juncture it is important not to lose focus on the present preparation and self-motivate yourself. Following 5 mantras each for students and parents will help a lot to avoid such situations.

FIVE MANTRAS FOR STUDENTS

1. Talk regularly to your parents. Many aspirants find refuge from parental pressure by reducing communication with them, but instead one must indulge in regular interactions. This will help a lot.
2. Never lied to them about anything. Even tell them you're below par performances and try to accept your failures as your motivation and inspiration. One of my student's was in the habit of sticking all his failures around his study table. According to him these failures always motivate him to do better. Today he is a successful Engineer in Armed Forces.
3. Try to listen them carefully and at the same time you may put your views also but in assertive manner only.
4. **There is the possibility that the views of your parents and you may not match.** In such a case the acceptability at both the ends is necessary e.g., I cannot impose my opinion about chemistry on my son. He may have a different perception about this subject according to his strength or weaknesses. So as a parent it's my duty to listen and understand his perception about this subject too.
5. **Most of your views may contradict with your parents.** This may be due to generation gap or anything else. Try to be open with your parents. Discuss your problems openly to seek their guidance and support.

FIVE MANTRAS FOR PARENTS

1. The support of parents can create wonders for anybody. It is really important for parents not to make their child realise that IIT JEE is the end of the world. Such a realisation creates a mental pressure in student's mind, which very

soon becomes a metal block. Formation of this block is tough to overpower and creates a great hindrance in their studies.

2. Secondly, do not impose too much of restrictions on your child. This may direct them towards revolt or non-cordial relations. These non-cordial relations do not holds good and create stress, frustration and finally reflect upon the academic performance along with mental and social health of the student. In such a situation instead of scolding and screaming out in frustration, both sides should discuss their differences with open minds.
3. In my opinion **parents should recommend but not command**; after all, one cannot clear IIT JEE until and unless he/she is self-motivated towards the goal. All that required is a balance between ‘**parental guidance**’ and ‘**parental pressure**’.
4. While I say that parents should avoid unnecessary interference, it is also important for them to maintain regular touch with their ward, keep records of all tests and ask for explanations for each performance. It is widely accepted that most parents cannot directly help in the studies of their ward but their moral support is very important. At an age when the child is most vulnerable to get misled, parental support is the only thing that can keep things on the right track.
5. Try to develop an ignorance factor as well for your ward. Mix this wisely with your check or restrictions in controlling your ward. Such a mixing always creates positive impact of your actions on your ward's mind.

Remember!

No relation can be as strong as a ‘parent-child’ relation. It's only your parents and teachers who selflessly wish for your best. Understand their motive of constantly pushing you to study, enquiring about your status in school and coaching, imposing ‘restrictions’ upon you or any other action on their part which supposedly ‘irritates’ you. Develop a mutual understanding with them which will help you not just in clearing IIT JEE but also in your future ventures.

Further, always keep following great lines of ANNE FRANK in your mind

“Parents can only give good advice or show the right path, but the final forming of a person's character lies in their own hands”

Formulae Used to Convert Amount of Substance into Moles

$$\text{Number of moles of molecules} = \frac{\text{Weight (in gram)}}{\text{Molecular weight}}$$

$$\text{Number of moles of atoms} = \frac{\text{Weight (in gram)}}{\text{Atomic weight}}$$

$$\text{Number of moles} = \frac{\text{Number of particles}}{\text{Avogadro's number}}$$

$$\text{Number of moles of gases} = \frac{\text{Volume of gas at STP (in L)}}{22.4 (\text{L mol}^{-1})}$$

Concentration Terms

- (a) **Normality (N)** It is defined as the number of gram equivalents of solute present in 1 L solution.

$$\begin{aligned} \text{Thus, } N &= \frac{\text{gram-equivalent of solute}}{\text{Volume of solution (in L)}} \\ &= \frac{\text{gram-equivalent of solute}}{\text{Volume of solute (in mL)}} \times 1000 \end{aligned}$$

If specific gravity is given,

$$N = \frac{\text{specific gravity} \times \% \text{ strength} \times 10}{\text{Equivalent weight}}$$

- (b) **Molarity (M)** It is defined as the number of moles of solute present in 1 L of solution.

$$M = \frac{\text{Moles of solute}}{\text{Volume of solution (in L)}}$$

If specific gravity is given,

$$M = \frac{\text{Specific gravity} \times \% \text{ strength} \times 10}{\text{Molecular weight}}$$

- (c) **Formality (F)** It is practically same as molarity

$$F = \frac{\text{Gram formula mass}}{\text{Volume (in L)}}$$

- (d) **Molality (m)** It is defined as the number of moles of solute present in 1000 g or 1 kg of solution.

$$m = \frac{\text{Moles of solute}}{\text{Mass of solvent (in g)}} \times 1000$$

Balancing of Chemical Reaction

If a chemical reaction is not balanced, we can balance it by applying principle of atomic conservation (POAC). Let us take an example,

Example 1 Ammonia gas reacts with oxygen gas to form gaseous nitrogen monoxide, NO, and water vapour at 1000°C. Write the balanced equation for this reaction.

Sol. You may go through the following steps to balance the reaction mentioned in the problem :

Step I Write an unbalanced equation containing the correct molecular formulae of reactants and products.

Unbalanced equation is,



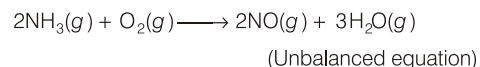
Step II Balance atoms of one of the elements.

Hydrogen is unbalanced, since there are three hydrogen atoms on the left and two on the right. Whenever, there are two and three atoms of hydrogen involved in the reaction, use coefficients to give six atoms on both sides. To do so, use a coefficient of 2 on the left and 3 on the right to get six hydrogen atoms on each side.

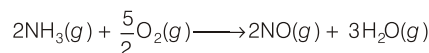


Step III Balance atoms of the remaining elements.

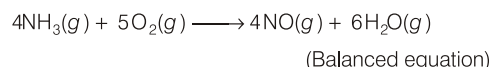
There are now two nitrogen atoms on the left and one on the right, so we balance nitrogen by using the coefficient 2 for the NO molecule.



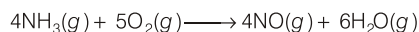
Now, there are two oxygen atoms on the left and five on the right. We use a coefficient of $\frac{5}{2}$ to balance the atoms of O₂.



The equation is now balanced, but it is customary to use whole number coefficients. Therefore, we multiply all the coefficients by 2 to get the final balanced equation.



Step IV Verify that the number of atoms of each element is balanced.



$$4\text{N} = 4\text{N}$$

$$12\text{H} = 12\text{H}$$

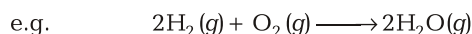
$$10\text{O} = 4\text{O} + 6\text{O}$$

Limiting Reagent

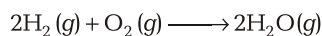
The reactant that is completely consumed in a reaction is called either the **limiting reactant** or **limiting reagent** because it determines, or limits, the amount of product formed. The other reactants are sometimes called either **excess reactants** or **excess reagents**.

Percentage excess

$$= \frac{\text{Moles in excess}}{\text{Moles require to react with limiting reagent}} \times 100$$



Let, initial quantities are taken as 10 and 7 moles of H₂(g) and O₂(g) respectively. H₂(g) and O₂(g) react to form water.

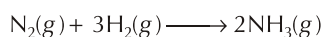
 CHEMISTRY CONCENTRATE


Initial quantities	10 mol	7 mol	0 mol
Quantities that are reacted	10 mol	- 5 mol	+ 10 mol
Final quantities	0 mol	2 mol	10 mol

Hence, H_2 is the limiting reagent, which means that once all the H_2 has been consumed, the reaction stops. O_2 is the excess reactant, and some is left over when the reaction stops.

Example 2

The formation of ammonia is given by the following reaction,



How many moles of NH_3 can be formed from 3.0 moles of N_2 and 6.0 moles of H_2 ?

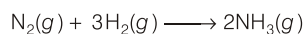
Sol. For calculation of limiting reagent, we will assume that one reactant is completely consumed, then we can calculate how much of the second reactant needed.

From the given reaction,

\therefore 1 mole of $\text{N}_2(\text{g})$ requires 3 moles of H_2 to give 2 moles of NH_3 .

\therefore 3 moles of N_2 will require $(3 \times 3 = 9)$ moles H_2 to give $(2 \times 3 = 6)$ moles of NH_3 .

But we have only 6.0 moles of $\text{H}_2(\text{g})$. Hence, $\text{H}_2(\text{g})$ is limiting reagent.



Initial quantities	3.0 mol	6.0 mol	0 mol
Reacted quantities	-2 mol	-6.0 mol	4.0 mol
Final quantities	1.0 mol	0 mol	4.0 mol

Hence, we shall calculate amount of ammonia with respect to limiting reagent.

\therefore 3 moles of $\text{H}_2(\text{g})$ give 2 moles of ammonia.

\therefore 6 moles of $\text{H}_2(\text{g})$ will give $\frac{2}{3} \times 6 = 4$ moles of ammonia

Hence, number of moles of ammonia formed
= 4

Different Kinds of Stoichiometric Problems

Stoichiometric problems may be classified into the following relationships:

Mass-Mass Relationship

When the reactants are given in terms of moles and moles of products are asked to find and *vice-versa*, we use mass-mass relationship in the chemical reaction.

Strategies to Solve Problems Related to Mass-Mass Relationship

These problems can be solved by the following methods:

(a) Mole method You can go through following steps:

Step I Write the complete balanced chemical reaction concerned in the problem.

Step II The stoichiometric coefficients in the balanced chemical reactions represent the relative number of moles of different reaction components. Relate the amounts of the reaction components concerned with the help of mole.

Step III Calculate the unknown amount of substance using unitary method.

Unitary Method

- Write down all number of moles of reactants and products in balanced chemical equation.
- From balanced equation, we get the information about number of moles of reactant used and product formed in the chemical reaction.
- Find out the number of moles of product formed from 1 mol of reactant, for this, divide the number of moles of products with number of moles of reactant in chemical equation.
- If from x mole of reactant, amount of product is asked, multiply x to the amount obtained for 1 mole of reactant.

Similarly, this method can be applied for mass (m) volume (V), and pressure (p) also.

(b) Principle of Atomic Conservation (POAC) Method

By this method, reactions are balanced by conserving the atoms of each element, the mole of atoms of each element in the reactant side should be equal to that in product side.

On applying the conservation of atoms of each element with the help of mole, we may get relations needed to solve the problem.

(c) Factor-label method Follow the steps given below :

Step I Convert the given amount of substance into its moles.

Step II Relate the moles of given substance with the moles of required substance as per balanced chemical equation or atomic conservation.

Step III Finally, convert the moles into the amount of the required substance.

(d) Equivalent method You can apply the following concept for solving the problem:

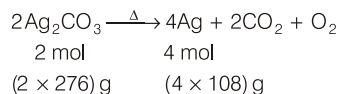
The number of gram-equivalents of each reactant reacted will be same and the same number of gram-equivalents of each products will form.

Example 3

2.76 g of silver carbonate on being strongly heated yield a residue weighing

- (a) 2.16 g (b) 2.48 g (c) 2.64 g (d) 2.32 g

Sol. (a) Mole-method



$\therefore (2 \times 276) \text{ g of Ag}_2\text{CO}_3 \text{ give Ag} = (4 \times 108) \text{ g}$

$$\therefore 1 \text{ g of Ag}_2\text{CO}_3 \text{ will give Ag} = \left(\frac{4 \times 108}{2 \times 276} \right) \text{ g}$$

$$\begin{aligned} \therefore 2.76 \text{ g of Ag}_2\text{CO}_3 \text{ will give Ag} \\ = \left(\frac{4 \times 108 \times 2.76}{2 \times 276} \right) \text{ g} \\ = 2.16 \text{ g} \end{aligned}$$

POAC Method

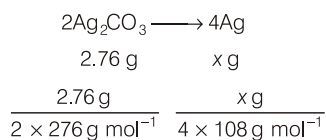
Moles of Ag in Ag_2CO_3 = Total moles of Ag as product

$$\text{or } 2 \times \text{moles of Ag}_2\text{CO}_3 = 4 \times \text{moles of Ag}$$

$$\text{or } (2 \times 276) \text{ g of Ag}_2\text{CO}_3 = (4 \times 108) \text{ g of Ag}$$

$$\text{or } 1 \text{ g of Ag}_2\text{CO}_3 = \left(\frac{4 \times 108}{2 \times 276} \right) \text{ g of Ag}$$

$$\begin{aligned} \text{or } 2.76 \text{ g of Ag}_2\text{CO}_3 &= \left(\frac{4 \times 108 \times 2.76}{2 \times 276} \right) \text{ g of Ag} \\ &= 2.16 \text{ g of Ag} \end{aligned}$$

Factor Label Method

$$\text{or } \frac{2.76}{2 \times 276} = \frac{x}{4 \times 108}$$

$$\begin{aligned} \text{or } x &= \frac{4 \times 108 \times 2.76}{2 \times 276} \\ &= 2.16 \text{ g} \end{aligned}$$

Equivalent Method

Number of gram-equivalents of Ag_2CO_3
= Number of gram-equivalents of Ag

$$\frac{2.76 \text{ g}}{\left(\frac{2 \times 276 \text{ g mol}^{-1}}{1} \right)} = \frac{x \text{ g}}{\left(\frac{4 \times 108 \text{ g mol}^{-1}}{1} \right)}$$

Here, 1 on LHS and RHS is change in oxidation state of Ag in Ag_2CO_3 and Ag, respectively

$$\therefore x = 2.16 \text{ g}$$

Per cent Yield

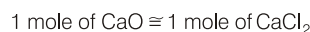
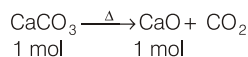
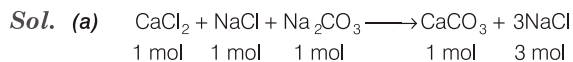
Generally, when a reaction is carried out in the laboratory, we do not obtain the theoretical amount of the product. The amount of the product that actually obtained is called the actual yield. Per cent yield can be calculated as

$$\text{Per cent yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

Example 4

A mixture of CaCl_2 and NaCl weighing 4.44 g is treated with sodium carbonate solution to precipitate all the Ca^{2+} ions as calcium carbonate. The calcium carbonate so obtained is heated strongly to get 0.56 g of CaO . The percentage of NaCl in the mixture (atomic mass of $\text{Ca} = 40$) is

- (a) 75 (b) 30.6 (c) 25 (d) 69.4



$$\frac{0.56}{56} \text{ mol of CaO} \equiv 0.01 \text{ mol of CaCl}_2 = 0.01 \times 111 \text{ g of CaCl}_2$$

$$= 1.11 \text{ g of CaCl}_2$$

Thus, in the mixture, weight of $\text{NaCl} = 4.44 - 1.11 = 3.33 \text{ g}$

$$\therefore \text{Percentage of NaCl} = \frac{3.33}{4.44} \times 100 = 75\%$$

Per cent Purity

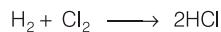
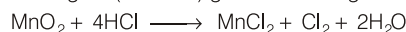
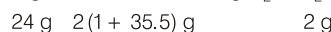
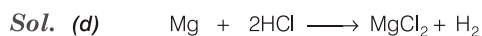
Generally, when we do experiments in the laboratory, the product we get *via* chemical reaction is not pure. It contains some amounts of reactants or other products or both as impurities. We can find the per cent purity by following formula,

$$\text{Per cent purity} = \frac{\text{Weight of reactant required}}{\text{Weight of reactant taken}} \times 100$$

Example 5

Chlorine evolved by the reaction of 45.31 g of pyrolusite (impure) and excess of HCl is found to combine completely with hydrogen produced by the reaction of 10 g of magnesium and excess of dilute hydrochloric acid. Find the percentage purity of MnO_2 in the given pyrolusite.

- (a) 98 (b) 95 (c) 70 (d) 80



2 g of hydrogen is obtained by using 24 g of Mg and 71 g of Cl_2 is obtained by 87 g of MnO_2 . The produced H_2 combines with 71 g of Cl_2 .

Thus, when 10 g of Mg is used, the mass of pure MnO_2 required

$$= \left(\frac{87}{24} \times 10 \right) \text{ g} = 36.25 \text{ g}$$

Hence, 45.31 g of pyrolusite contains MnO_2 (pure) = 36.25 g

$$\therefore 100 \text{ g of pyrolusite contain MnO}_2 \text{ (pure)} = \frac{36.25}{45.31} \times 100 = 80.004 \text{ g}$$

$$\therefore \text{Percentage purity} = 80\%$$

CHEMISTRY CONCENTRATE

Volume-Volume Relationship

When both the reactants and products are gases and are given in terms of volume, we use volume-volume relationship to solve the problem.

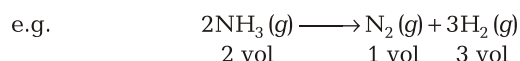
These calculations are based on two laws:

- (i) Avogadro's law (ii) Gay Lussac's law

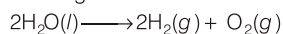
Avogadro's law At constant pressure (p) and temperature (T), the volume (V) of a gas is proportional to the number of moles (n) of gaseous species present in a container.

$$V \propto n$$

Gay-Lussac's law Under similar conditions of temperature and pressure, volume of gases taking part in a chemical reaction show simple whole number ratios to one another.



Note When liquid water undergoes electrolysis to produce hydrogen gas and oxygen gas, the volumes of hydrogen gas to oxygen gas are produced in 2 : 1 ratio. But volume of liquid water does not follow Gay-Lussac's relationship of volumes as liquid water is not a gas



Volume versus Mass for Stoichiometry in Relation to Gases

- For solids and liquids, it is easy to establish laws on chemical combinations by taking masses of the substances involved in the chemical reactions.
- Masses of solids and liquids do not change appreciably with change in temperature and pressure.
- Gases are sensitive towards changes in temperature and pressure. Hence, we use term volume in order to explain laws of chemical combinations for gases.
- Pressure and temperature are interconnected to each other, i.e. if pressure increases temperature also increases.
- Volume can be increased by decrease in pressure or it can be decreased by increase in pressure.
- Gases expand or contract with increase or decrease in temperature respectively.
- There are fixed number of molecules or atoms of any gas in a fixed volume at standard temperature and pressure (STP) conditions.

Note At STP, the value of gaseous molar volume is 22.4 L or 22400 mL or 22400 cc.

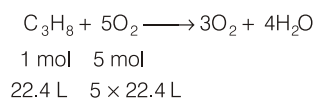
Example 6

What volume of oxygen gas (O_2) measured at 0°C and 1 atm, is needed to burn completely 1 L of propane gas (C_3H_8) measured under the same conditions?

- (a) 2 L (b) 6 L (c) 5 L (d) 10 L

Sol. (c) Volume of 1 mole of a gas at STP = 22.4 L [as $V \propto n$]

The combustion reaction of propane is given as



\therefore To burn 22.4 L C_3H_8 , the oxygen required

$$= 5 \times 22.4 \text{ L}$$

\therefore To burn 1 L C_3H_8 , the oxygen required will be

$$= \frac{5 \times 22.4}{22.4} = 5 \text{ L}$$

Mass-Volume Relationship

When the reactants are given in terms of mass and volume of products formed is asked to find and *vice-versa*, we use the combined mass-volume relationship.

We can also use ideal gas equation to interconvert mole, mass and volume and it is given as,

$$pV = nRT = \frac{m}{M} RT$$

where, p , V and T are pressure, volume and temperature respectively. m and M are mass and molecular/atomic mass of reactant or product respectively.

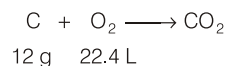
Example 7

40 g of a sample of carbon on combustion left 10% of it unreacted. The volume of oxygen required at STP for this combustion reaction is

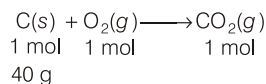
- (a) 22.4 L (b) 67.2 L
(c) 11.2 L (d) 44.8 L

Sol. (b) You can go through the following steps:

Step I Write down the balanced chemical reaction



Step II Write down the mass-volume relationship for the chemical equation,



Step III Find out the limiting reagent. As 10%,

i.e. $\left(40 \times \frac{10}{100} = 4 \text{ g}\right)$ of sample of carbon left unreacted. Hence,

O_2 acts as a limiting reagent.

Step IV Find out volume of O_2 at STP

At STP, for the combustion of 12 g of C, oxygen required = 22.4 L

\therefore For the combustion of 36 g of C, oxygen required will be

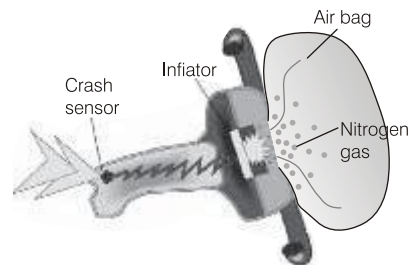
$$= \frac{22.4}{12} \times 36 \text{ L}$$

$$= 67.2 \text{ L}$$

Smart Practice

- If 0.50 mole of BaCl_2 is mixed with 0.20 mole of Na_3PO_4 , then maximum number of moles of $\text{Ba}_3(\text{PO}_4)_2$ that can be formed is
 (a) 0.70 (b) 0.50
 (c) 0.20 (d) 0.10
 - Air contains 20% oxygen by volume. Calculate the theoretical volume of air which will be required for burning 200 m^3 of acetylene gas completely. All volumes are measured under the same conditions of temperature and pressure.
 (a) 2500 m^3 (b) 2000 m^3
 (c) 1500 m^3 (d) 1000 m^3
 - How many grams of CaO are required to neutralise 852 g of P_4O_{10} ?
 (a) 1000 g (b) 1050 g
 (c) 1008 g (d) 1090 g
 - A cylinder of compressed gas contains nitrogen and oxygen in the ratio of 3 : 1 by mole. If the cylinder is known to contain 2.5×10^4 g of oxygen, what is the total mass of the gas mixture?
 (a) 2.07×10^5 g
 (b) 6.03×10^4 g
 (c) 8.02×10^5 g
 (d) 9.06×10^4 g
 - $\text{A} + 2\text{B} + 3\text{C} \rightleftharpoons \text{AB}_2\text{C}_3$
 Reaction of 6.0 g of A, 6.0×10^{23} atoms of B and 0.036 mole of C yield 4.8 g of compound AB_2C_3 . If the atomic masses of A and C are 60 and 80u, respectively, the atomic mass of B is (Avogadro's number = 6.0×10^{23})
 (a) 50 u (b) 60 u
 (c) 70 u (d) 40 u
 - How much $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and pure water are to be mixed to prepare 50 g of 12.0% (by mass) BaCl_2 solution?
 (a) 40.4 g (b) 42.9 g
 (c) 52.7 g (d) 50.0 g
 - A sample of green crystals of nickel (II) sulphate heptahydrate was heated carefully to produce the bluish-green nickel (II) sulphate hexahydrate. If 8.753 g of the heptahydrate produces 8.192 g of the hexahydrate, how many gram of anhydrous nickel (II) sulphate could be obtained?
 (a) 2.413 g (b) 0.206 g (c) 1.604 g (d) 4.826 g
 - Match the following columns.
- | Column I
(Reaction) | Column II
(Mass of product) |
|--|--------------------------------|
| A. $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$
1 g 1 g ? | p. 1.214 g |
| B. $\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2$
1 g ? | q. 1.125 g |
| C. $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$
1 g 1 g ? | r. 1.333 g |
| D. $\text{C} + 2\text{H}_2 \longrightarrow \text{CH}_4$
1 g 1 g ? | s. 0.560 g |
- Codes**
- | | |
|-------------|-------------|
| A B C D | A B C D |
| (a) p q r s | (b) q p s r |
| (c) p s q r | (d) r s q p |
- A 2 g of a sample containing sodium carbonate and sodium bicarbonate was heated to a temperature at which all the sodium bicarbonate in the sample was converted to sodium carbonate, CO_2 and H_2O . The final weight of sample after heating becomes 1.752 g. The percentage of Na_2CO_3 in the sample is
 (a) 76% (b) 66% (c) 72% (d) 54%
 - 1L of oxygen at NTP reacts with 3 L of carbon monoxide at NTP. Calculate the ratio of volume of carbon monoxide to that of carbon dioxide after the completion of the reaction.
 (a) 1 : 2 (b) 2 : 3 (c) 1 : 4 (d) 2 : 1

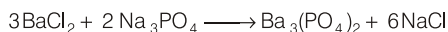
Automotive airbags contain the supremely toxic salt sodium azide NaN_3 . In the event of a collision, a signal from the vehicle's deceleration sensors trigger an electrical impulse which raises the temperature around the salt dramatically, causing it to decompose into harmless nitrogen gas N_2 which rapidly expands into the airbag.



**AMAZING
REALITIES**

Answers with Explanation

1. (d) The balanced chemical reaction is



In this reaction, 3 moles of BaCl_2 combines with 2 moles of Na_3PO_4 . Hence, 0.5 mole of BaCl_2 will require $\frac{2}{3} \times 0.5$

$$= 0.33 \text{ mole of } \text{Na}_3\text{PO}_4$$

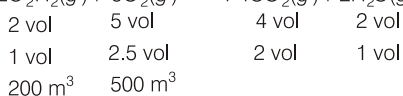
Since, available Na_3PO_4 (0.2 mole) is less than the required mole (0.33), it is the limiting reagent and will determine the amount of product $\text{Ba}_3(\text{PO}_4)_2$.

\therefore 2 moles of Na_3PO_4 give 1 mole of $\text{Ba}_3(\text{PO}_4)_2$.

\therefore 0.2 mole of Na_3PO_4 will give = $\frac{1}{2} \times 0.2$

$$= 0.1 \text{ mole of } \text{Ba}_3(\text{PO}_4)_2$$

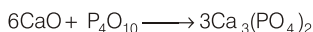
2. (a) $2\text{C}_2\text{H}_2(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 4\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$



As 500 m³ of O_2 is required for complete combustion of 200 m³ of C_2H_2 . Since, 20 m³ of O_2 is present in 100 m³ of air, therefore 500 m³ of O_2 will present in volume of air

$$= \left(\frac{100}{20} \times 500 \right) \text{m}^3 = 2500 \text{m}^3$$

3. (c) The reaction involved is



Molecular weight of P_4O_{10}

$$= (31 \times 4 + 16 \times 10) \text{g mol}^{-1}$$

$$= 284 \text{g mol}^{-1}$$

Number of moles of P_4O_{10}

$$= \frac{852 \text{g}}{284 \text{g mol}^{-1}} = 3 \text{mol}$$

As 1 mole of P_4O_{10} neutralises 6 moles of CaO .

\therefore 3 moles of P_4O_{10} will neutralise 18 moles of CaO .

\therefore Mass of $\text{CaO} = (18 \times 56) \text{g} = 1008 \text{g}$

4. (d) Number of moles of oxygen in the cylinder

$$= \frac{\text{Mass (in g)}}{\text{Molecular mass (in g)}} = \frac{2.5 \times 10^4}{32}$$

$$= 781.25$$

Number of moles of N_2 in the cylinder

$$= 3 \times 781.25 = 2343.75 \quad [\text{as } \text{N} : \text{O} = 3 : 1]$$

Mass of nitrogen in the cylinder

$$= 2343.75 \text{mol} \times 28 \text{g mol}^{-1} = 65625 \text{g}$$

$$= 6.56 \times 10^4 \text{g}$$

\therefore Total mass of the gas in the cylinder

$$= (2.5 \times 10^4 + 6.56 \times 10^4) \text{g}$$

$$= 9.06 \times 10^4 \text{g}$$

5. (a) $\text{A} + 2\text{B} + 3\text{C} \longrightarrow \text{AB}_2\text{C}_3$... (i)

Given, 6.0 g of A, 6.0×10^{23} atoms of B and 0.036 mole of C yield 4.8 g of compound AB_2C_3 .

Atomic mass of A = 60 u

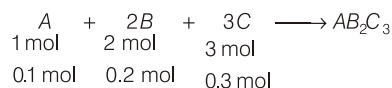
Atomic mass of C = 80 u

$$\text{Mole of A} = \frac{6}{60} = \frac{1}{10} = 0.1 \text{ mol}$$

$$\text{Mole of B} = \frac{6.0 \times 10^{23}}{6.0 \times 10^{23}} = 1 \text{ mol}$$

Mole of C = 0.036 mol

Now, from Eq. (i),



But we have 0.036 mole of C, Hence, C is the limiting reagent

From Eq. (i),

3 moles of C produce 1 mole of AB_2C_3 .

\therefore 0.036 moles of C will produce $\left(\frac{1}{3} \times 0.036 \right)$ mole of AB_2C_3 ,

i.e. 0.012 mole of AB_2C_3 .

Now, number of moles of

$$\text{AB}_2\text{C}_3 = \frac{\text{Mass of } \text{AB}_2\text{C}_3 \text{ (in g)}}{\text{Molecular mass of } \text{AB}_2\text{C}_3}$$

$$0.012 = \frac{4.8}{\text{Molecular mass of } \text{AB}_2\text{C}_3}$$

So, molecular mass of $\text{AB}_2\text{C}_3 = 400 \text{g mol}^{-1}$

i.e. Atomic mass of A + 2 (Atomic mass of B)

+ 3 (Atomic mass of C) = 400

or $60 + 2B + 3 \times 80 = 400$

or $B = 50 \text{u}$

6. (b) $w = 12 \text{g BaCl}_2$; $W = 100 \text{g}$ of solution

For 50 g of solution, $w = 6 \text{g BaCl}_2$;

$$W = 50 \text{g solution}$$

$$\therefore w_{\text{BaCl}_2 \cdot 2\text{H}_2\text{O}} = \left(\frac{6 \times 244}{208} \right) \text{g} \quad [\text{BaCl}_2 \approx \text{BaCl}_2 \cdot 2\text{H}_2\text{O}]$$

$$= 7.038 \text{g}$$

$$w_{\text{H}_2\text{O}} = (50 - 7.038) \text{g}$$

$$= 42.962 \text{g} \approx 42.9 \text{g}$$

7. (d) $\text{NiSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow{\Delta} \text{NiSO}_4 \cdot 6\text{H}_2\text{O} \xrightarrow{\Delta} \text{NiSO}_4$
(Green) (Bluish green)

Let, molar mass of NiSO_4 is a, mole ratio of each is

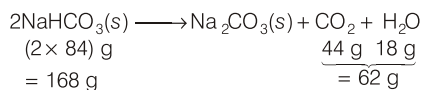
$$\frac{8.753}{(a + 126)} = \frac{8.192}{(a + 108)} = \frac{w}{a} \quad [w = \text{mass of } \text{NiSO}_4]$$

$$w = 4.826 \text{g}$$

8. (c)

Reaction	Limiting reagent	Mass of product
$\begin{array}{c} \text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3 \\ 1 \text{ g} \quad 1 \text{ g} \\ \frac{1}{28} \text{ mol} \quad \frac{1}{2} \text{ mol} \end{array}$	N ₂	$\begin{aligned} \frac{1}{28} \text{ mol N}_2 &\equiv \frac{1}{14} \text{ mol} \\ \text{NH}_3 &\equiv \frac{1}{14} \times 17 \text{ g} \\ &= 1.214 \text{ g} \end{aligned}$
$\begin{array}{c} \text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2 \\ 1 \text{ g} \\ \frac{1}{100} \text{ mol} \quad \frac{1}{100} \text{ mol} \quad \frac{1}{100} \text{ mol} \end{array}$	—	$\begin{aligned} \left(\frac{1}{100} \times 56 \right) \text{ g of CaO} \\ = 0.56 \text{ g of CaO} \end{aligned}$
$\begin{array}{c} 2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O} \\ 1 \text{ g} \quad 1 \text{ g} \\ \frac{1}{2} \text{ mol} \quad \frac{1}{32} \text{ mol} \end{array}$	O ₂	$\begin{aligned} 1 \text{ mol O}_2 &\equiv 2 \text{ mol H}_2\text{O} \\ \frac{1}{32} \text{ mol O}_2 &\equiv \frac{1}{16} \text{ mol H}_2\text{O} \\ &\equiv \frac{18}{16} \text{ g of H}_2\text{O} \\ &= 1.125 \text{ g H}_2\text{O} \end{aligned}$
$\begin{array}{c} \text{C} + 2\text{H}_2 \longrightarrow \text{CH}_4 \\ 1 \text{ g} \quad 1 \text{ g} \\ \frac{1}{100} \text{ mol} \quad \frac{1}{2} \text{ mol} \end{array}$	C	$\begin{aligned} \frac{1}{12} \text{ mol C} &\equiv \frac{1}{12} \text{ mol CH}_4 \\ &\equiv \frac{16}{12} \text{ g CH}_4 \\ &\equiv 1.333 \text{ g CH}_4 \end{aligned}$

9. (b) The chemical reaction occurred after heating the sample can be written as



Here, the weight loss by the sample is due to evolution of CO₂ and H₂O.

∴ Weight of CO₂ and H₂O evolved = (2 – 1.752) g = 0.248 g
62 g of CO₂ and H₂O are produced by 168 g of NaHCO₃.

∴ 0.248 g of CO₂ and H₂O will be produced by the mass of

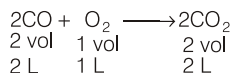
$$\text{NaHCO}_3 = \left(\frac{168}{62} \times 0.248 \right) \text{ g} = 0.672 \text{ g NaHCO}_3$$

∴ Weight of NaHCO₃ in the sample = 0.672 g

∴ Weight of Na₂CO₃ = (2 – 0.672) g = 1.328 g

∴ % of Na₂CO₃ = $\frac{1.328 \times 100}{2} = 66\%$

10. (a) The balanced chemical reaction is



Here, 1 L of O₂ reacts with 2 L of CO. Hence, 1 L of CO remains unreacted at the end of the reaction.

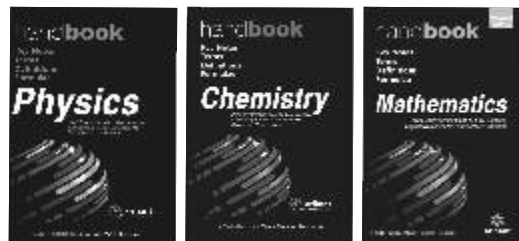
Hence, volume of CO at the end of the reaction is 1 L.

Also, 1 L of O₂ will produce 2 L of CO₂. So, volume of CO₂ at the end of the reaction = 2 L

$$\frac{V_{\text{CO}}}{V_{\text{CO}_2}} = \frac{1}{2} = 1 : 2$$

handbook

KEY NOTES | TERMS
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JEE MAIN 2016

PAPER I (Online)

FULLY SOLVED

EXAM CRUX

In Chemistry, there were total 30 Questions asked in JEE Main (Online) 2016 paper. Out of which, 8 were numericals, while 22 questions were theory based. Overall paper was tricky and easy to solve.

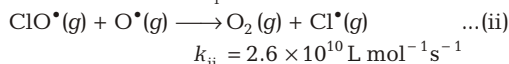
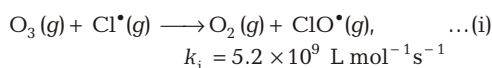
According to chapterwise distribution, number of questions were asked as

- **From Class XI** Some Basic Principles of Organic Chemistry-3Qs, Hydrocarbons-2Qs, s-block Elements-2Qs, Atomic Structure-2Qs, States of Matter-1Q, Thermodynamics, Equilibrium, Hydrogen and Chemical Bonding-1Q from each.
- **From Class XII** Metallurgy-3Qs, Chemistry in Everyday Life-2Qs, p-block Elements-2Qs, Solutions, Solid State, Chemical Kinetics, Surface Chemistry, Coordination Compounds, Alcohols, Phenols and Ethers, Amines-1Q from each.
- **Difficulty Level** Around 40% of questions can be considered as easy, 30% are relatively tough and 30% are considered to be tough by Arihant team. This year paper was little tough as compare to the previous year paper.

1. The artificial sweetener that has the highest sweetness value in comparison to cane sugar is
(a) Saccharin (b) Sucralose (c) Alitame (d) Aspartame

2. The non-metal that does not exhibit positive oxidation state is
(a) fluorine (b) oxygen (c) chlorine (d) iodine

3. The reaction of ozone with oxygen atoms in the presence of chlorine atoms can occur by a two step process shown below



The closest rate constant for the overall reaction $\text{O}_3(g) + \text{O}^\bullet(g) \longrightarrow 2\text{O}_2(g)$, is

- (a) $1.4 \times 10^{20} \text{ L mol}^{-1} \text{ s}^{-1}$ (b) $5.2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$
(c) $3.1 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ (d) $2.6 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$
4. 5 L of an alkane requires 25 L of oxygen for its complete combustion. If all volumes are measured at constant temperature and pressure, the alkane is
(a) butane (b) isobutane
(c) ethane (d) propane

5. Match the items in Column I with its main use listed in Column II.

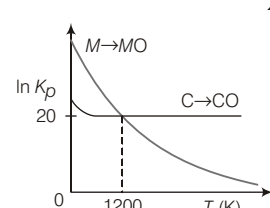
	Column I	Column II
A.	Silica gel	1. Transistor
B.	Silicon	2. Ion-exchanger
C.	Silicone	3. Drying agent
D.	Silicate	4. Sealant

Codes

	A	B	C	D		A	B	C	D
(a)	3	1	4	2	(b)	2	1	4	3
(c)	4	1	2	3	(d)	2	4	1	3

6. The group of molecules having identical shape is
(a) PCl_5 , IF_5 , XeO_2F_2 (b) BF_3 , PCl_3 , XeO_3
(c) ClF_3 , XeOF_2 , XeF_3^+ (d) SF_4 , XeF_4 , CCl_4
7. Which one of the following species is stable in aqueous solution?
(a) MnO_4^{2-} (b) MnO_4^{3-} (c) Cu^+ (d) Cr^{2+}
8. For the reaction, $A(g) + B(g) \longrightarrow C(g) + D(g)$, ΔH° and ΔS° are, respectively, $-29.8 \text{ kJ mol}^{-1}$ and $-0.100 \text{ kJ K}^{-1} \text{ mol}^{-1}$ at 298 K. The equilibrium constant for the reaction at 298 K is
(a) 1 (b) 10
(c) 1.0×10^{-10} (d) 1.0×10^{10}

- 9. Assertion** Rayon is a semisynthetic polymer whose properties are better than natural cotton.
Reason Mechanical and aesthetic properties of cellulose can be improved by acetylation.
 (a) Both Assertion and Reason are correct and Reason is the correct explanation for the Assertion
 (b) Both Assertion and Reason are incorrect
 (c) Assertion is incorrect statement, but Reason is correct
 (d) Both Assertion and Reason are correct, but the Reason is not the correct explanation for the Assertion
- 10.** The hydrocarbon with seven carbon atoms containing a neopentyl and a vinyl group is
 (a) 4, 4-dimethylpentene (b) 2, 2-dimethyl-4-pentene
 (c) isopropyl-2-butene (d) 2, 2-dimethyl-3-pentene
- 11.** The gas evolved on heating CH_3MgBr in methanol is
 (a) propane (b) ethane (c) HBr (d) methane
- 12.** Identify the correct trend given below
 (Atomic number, $\text{Ti} = 22$, $\text{Cr} = 24$ and $\text{Mo} = 42$)
 (a) Δ_o of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} < [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$
 and Δ_o of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} < [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$
 (b) Δ_o of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} > [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$
 and Δ_o of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} > [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$
 (c) Δ_o of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} > [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$
 and Δ_o of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} < [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$
 (d) Δ_o of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} < [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$
 and Δ_o of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} > [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$
- 13.** The most appropriate method of making egg-albumin sol is
 (a) keep the egg in boiling water for 10 minutes. After removing the shell, transfer the yellow part of the content to 100 mL of 5% w/V saline solution and homogenise with a mechanical shaker
 (b) break an egg carefully and transfer the transparent part of the content to 100 mL of 5% w/V saline solution and stir well
 (c) keep the egg in boiling water for 10 minutes. After removing the shell, transfer the white part of the content to 100 mL of 5% w/V saline solution and homogenise with a mechanical shaker
 (d) Break an egg carefully and transfer only the yellow part of the content to 100 mL of 5% w/V saline solution and stir well
- 14.** Which one of the following complexes will consume more equivalents of aqueous solution of AgNO_3 ?
 (a) $\text{Na}_3[\text{CrCl}_6]$ (b) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$
 (c) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (d) $\text{Na}_2[\text{CrCl}_5(\text{H}_2\text{O})]$
- 15.** At very high pressures, the compressibility factor of one mole of a gas is given by
 (a) $1 + \frac{pb}{RT}$ (b) $\frac{pb}{RT}$ (c) $1 - \frac{b}{VRT}$ (d) $1 - \frac{pb}{RT}$
- 16.** A reaction at 1 bar is non-spontaneous at low temperature but becomes spontaneous at high temperature.
 Identify the correct statement among the following.
 (a) Both ΔH and ΔS are positive
 (b) ΔH is negative while ΔS is positive
 (c) ΔH is positive while ΔS is negative
 (d) Both ΔH and ΔS are negative
- 17.** Which intermolecular force is most responsible in allowing xenon gas to liquefy?
 (a) Instantaneous dipole-induced dipole
 (b) Ionic
 (c) Ion-dipole
 (d) Dipole-dipole
- 18.** Identify the incorrect statement from the following regarding heavy water.
 (a) It reacts with CaC_2 to produce C_2D_2 and $\text{Ca}(\text{OD})_2$
 (b) It is used as a coolant in nuclear reactors
 (c) It reacts with Al_4C_3 to produce CD_4 and $\text{Al}(\text{OD})_3$
 (d) It reacts with SO_3 to form deuterated sulphuric acid (D_2SO_4)
- 19.** A particular adsorption process has the following characteristics. (a) It arises due to van der Waals' forces and (b) it is reversible.
 Identify the correct statement that describes the above adsorption process.
 (a) Enthalpy of adsorption is greater than 100 kJ mol^{-1}
 (b) Adsorption is monolayer
 (c) Adsorption increases with increase in temperature
 (d) Energy of activation is low
- 20.** The plot shows the variation of $-\ln K_p$ versus temperature for the two reactions.

$$\text{M}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{MO}(\text{s}) \quad \text{and} \quad \text{C}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}(\text{s})$$

 Identify the correct statement.
 (a) At $T > 1200 \text{ K}$, carbon will reduce $\text{MO}(\text{s})$ to $\text{M}(\text{s})$
 (b) At $T < 1200 \text{ K}$, oxidation of carbon is unfavourable
 (c) Oxidation of carbon is favourable at all temperatures
 (d) At $T < 1200 \text{ K}$, the reaction

$$\text{MO}(\text{s}) + \text{C}(\text{s}) \longrightarrow \text{M}(\text{s}) + \text{CO}(\text{g})$$
 is spontaneous
- 21.** BOD stands for
 (a) Biochemical Oxygen Demand
 (b) Biochemical Oxidation Demand
 (c) Biological Oxygen Demand
 (d) Bacterial Oxidation Demand
- 22.** What will occur if a block of copper metal is dropped into a beaker containing a solution of 1 M ZnSO_4 ?
 (a) The copper metal will dissolve and zinc metal will be deposited
 (b) The copper metal will dissolve with evolution of oxygen gas
 (c) The copper metal will dissolve with evolution of hydrogen gas
 (d) No reaction will occur

 EXAM SPECTRUM

23. The test to distinguish primary, secondary and tertiary amine is
 (a) mustard oil test (b) $C_6H_5SO_2Cl$
 (c) Sandmeyer's reaction (d) Carbylamine reaction
24. The total number of orbitals associated with the principal quantum number 5 is
 (a) 5 (b) 20 (c) 25 (d) 4
25. The correct order of the solubility of alkaline-earth metal sulphates in water is
 (a) $Mg < Sr < Ca < Ba$ (b) $Mg > Ca > Sr > Ba$
 (c) $Mg > Sr > Ca > Ba$ (d) $Mg < Ca < Sr < Ba$
26. An organic compound contains C, H and S. The minimum molecular weight of the compound containing 8% sulphur is (atomic weight of S = 32 amu)
 (a) 300 g mol^{-1} (b) 400 g mol^{-1}
 (c) 200 g mol^{-1} (d) 600 g mol^{-1}
27. Bouveault-Blanc reduction reaction involves
 (a) reduction of an anhydride with $LiAlH_4$
 (b) reduction of an ester with Na/C_2H_5OH
 (c) reduction of a carbonyl compound with Na/Hg and HCl
 (d) reduction of an acyl halide with H_2/Pd
28. Consider the following sequence for aspartic acid.
- $$\begin{array}{c}
 \text{CO}_2\text{H} \\
 | \\
 \text{H}_3\text{N}^+ - \text{C} - \text{H} \\
 | \\
 \text{CH}_2\text{CO}_2\text{H}
 \end{array}
 \xrightarrow[1.88]{pK_1}
 \begin{array}{c}
 \text{CO}_2^- \\
 | \\
 \text{H}_3\text{N}^+ - \text{C} - \text{H} \\
 | \\
 \text{CH}_2\text{CO}_2\text{H}
 \end{array}
 \xrightarrow[3.65]{pK_p}
 \begin{array}{c}
 \text{CO}_2^- \\
 | \\
 \text{H}_3\text{N}^+ - \text{C} - \text{H} \\
 | \\
 \text{CH}_2\text{CO}_2^-
 \end{array}$$
- $$\begin{array}{c}
 \text{CO}_2^- \\
 | \\
 \text{H}_2\text{N} - \text{C} - \text{H} \\
 | \\
 \text{CH}_2\text{CO}_2^-
 \end{array}
 \xrightarrow[9.60]{pK_2}
 \begin{array}{c}
 \text{CO}_2^- \\
 | \\
 \text{H}_2\text{N} - \text{C} - \text{H} \\
 | \\
 \text{CH}_2\text{CO}_2^-
 \end{array}$$
- The pI (isoelectric point) of aspartic acid is
 (a) 5.74 (b) 3.65 (c) 2.77 (d) 1.88
29. The amount of arsenic pentasulphide, that can be obtained when 35.5 g arsenic acid is treated with excess H_2S in the presence of conc. HCl (assuming 100% conversion), is
 (a) 0.25 mol (b) 0.125 mol
 (c) 0.333 mol (d) 0.50 mol
30. The solubility of N_2 in water at 300 K and 500 torr partial pressure is 0.01 g L^{-1} . The solubility (in g L^{-1}) at 750 torr partial pressure is
 (a) 0.02 (b) 0.015
 (c) 0.0075 (d) 0.005

Answers with Explanation

1. (c) Saccharin is about 300 to 400 times sweeter than sucrose.
 • Sucralose is about 320 to 1000 times sweeter than sucrose.
 • Alitame is about 2000 times sweeter than sugar.
 • Aspartame is about 200 times sweeter than sugar.
2. (a) In periodic table, fluorine is the most electronegative element. It shows only -1 oxidation state while other members of halogen family (Cl, I) show oxidation states from -1 to $+7$.
 Oxygen is a bivalent element because it has two unpaired electrons in its valence p -orbital. It does not have empty d -orbitals, thus could not expand its octet. Generally, oxygen exhibits -2 oxidation state, however it also exhibits $+2$ oxidation state in OF_2 , where fluorine atom is more electronegative than oxygen atom.
3. (a) **Key concept** When we add two or more chemical reactions to get a new chemical reaction, the rate constant for new chemical reaction will be equal to the multiplication of rate constants of corresponding reactions involved in addition.
 On adding Eq. (i) and Eq. (ii), we get,

$$O_3(g) + Cl^*(g) \longrightarrow O_2(g) + ClO^*(g) \quad \dots(i)$$

$$ClO^*(g) + O^*(g) \longrightarrow O_2(g) + Cl^*(g) \quad \dots(ii)$$

$$O_3(g) + ClO^*(g) + Cl^*(g) + O^*(g) \longrightarrow 2O_2(g) + ClO^*(g) + Cl^*(g)$$

$$O_3(g) + O^*(g) \longrightarrow 2O_2(g) \quad \dots(iii)$$
 For Eq. (iii), rate constant (k) = $k_i \times k_{ii}$

$$= (5.2 \times 10^9) \times (2.6 \times 10^{10})$$

$$= 1.35 \times 10^{20} \text{ L mol}^{-1}\text{s}^{-1}$$

$$\approx 1.4 \times 10^{20} \text{ L mol}^{-1}\text{s}^{-1}$$
4. (d) Let, alkane be C_nH_{2n+2} .
 The reaction involving combustion is given as,

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

$$\begin{array}{cccc}
 1 \text{ mol} & \left(\frac{3n+1}{2}\right) \text{ mol} & n \text{ mol} & (n+1) \text{ mol} \\
 5 \text{ L} & 25 \text{ L} & &
 \end{array}$$
 From ideal gas equation,

$$pV = n'RT$$
 In the problem, p and T are given as constants. Hence,
 $V \propto n'$; (R = gas constant, n' = gaseous moles)
 or $V = n'K \quad \dots(i)$
 (K = Proportionality constant)
 On applying Eq. (i) for alkane and oxygen,
 For alkane, $5 = K (n' = 1)$
 For oxygen, $25 = \left(\frac{3n+1}{2}\right)K$
 or $25 = \left(\frac{3n+1}{2}\right) \times 5$
 or $n = 3$
 \therefore Alkane is $C_nH_{2n+2} = C_3H_8$ (Propane)
5. (a)
6. (c) **Strategy** Generally, the molecules in which same number of atoms and lone pairs are attached to the central atom, possess same shape.



For option (a), atoms attached to the central atom are different. So, we will check this option in the last if needed.

For option (b), atoms attached to the central atom are same, so we will check for lone pairs.

Molecule	Lone pair
	Zero
	One
	One

Hence, option (b) is incorrect.

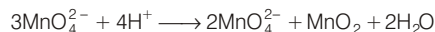
For option (c), atoms attached to central atom are same. Again, we will check for lone pairs.

Molecule	Lone pair	Shape
	Two	T-shaped
	Two	T-shaped
	Two	T-shaped

Hence, option (c) is correct.

We don't need to check option (d) because of saving time purpose.

7. (a) MnO_4^{2-} does not dissociate in aqueous solution. It dissociates in neutral or acidic solution.



8. (a) For equilibrium constant, first we shall calculate ΔG° .

$$\begin{aligned} \Delta G^\circ \text{ is given as, } \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -29.8 - 298(-0.100) \\ &= -29.8 + 29.8 \end{aligned}$$

$$\therefore \Delta G^\circ = 0$$

Now as we know,

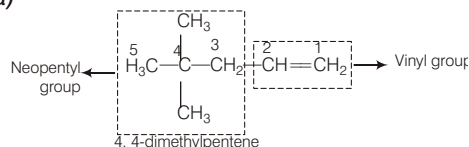
$$\begin{aligned} \Delta G^\circ &= -RT \ln K_{\text{eq}} \\ 0 &= -RT \ln K_{\text{eq}} \end{aligned}$$

$$\text{or } \ln K_{\text{eq}} = 0$$

$$\text{or } K_{\text{eq}} = e^0 = 1$$

9. (a) Rayon is manufactured from naturally occurring polymers (cellulose fibre from wood pulp). It is improved by acetylation of cellulose.

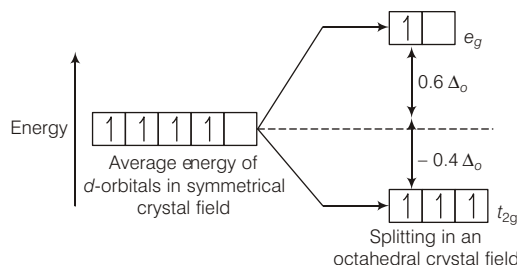
10. (a)



11. (d) $\text{CH}_3\text{MgBr} + \text{CH}_3\text{OH} \longrightarrow \text{CH}_3\text{O}(\text{MgBr}) + \text{CH}_4 \uparrow$
Methane

12. (b) For $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$

$$\text{Cr}^{2+} = [\text{Ar}], 3d^4$$



As, H_2O is a weak field ligand, so pairing of electrons does not occur.

$$\text{CFSE for } [\text{Cr}(\text{H}_2\text{O})_6]^{2+} = 3(-0.4\Delta_o) + 1(0.6\Delta_o) = -0.6\Delta_o$$

Similarly,

Complex	Metal ion	Electronic configuration	CFSE
$[\text{Mo}(\text{H}_2\text{O})_6]^{2+}$	Mo^{2+}	t_{2g}^3, e_g^1	$-0.6\Delta_o$
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	Ti^{3+}	t_{2g}^3, e_g^0	$-0.4\Delta_o$
$[\text{Ti}(\text{H}_2\text{O})_6]^{2+}$	Ti^{2+}	t_{2g}^2, e_g^0	$-0.8\Delta_o$

$\Delta_o \propto \text{Crystal Field Stabilisation Energy (CFSE)}$

Δ_o depends on Z_{eff} and for $3d$ -series, Z_{eff} is less than $4d$ -series.

$$\text{Hence, } \Delta_o \text{ of } [\text{Cr}(\text{H}_2\text{O})_6]^{2+} > [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$$

From above table,

$$\Delta_o \text{ of } [\text{Ti}(\text{H}_2\text{O})_6]^{3+} > \Delta_o \text{ of } [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$$

13. (b) The transparent part of egg contains albumin.

14. (c) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ contains maximum number of ionisable anion (3Cl^-). Hence, it will consume more equivalents of aqueous solution of AgNO_3 and forms three moles of AgCl (white ppt.).

Complex	Dissociation in aqueous solution of AgNO_3
$\text{Na}_3[\text{CrCl}_6]$	$3\text{Na}^+ + [\text{CrCl}_6]^{3-}$
$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$	$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+} + 2\text{Cl}^-$
$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+} + 3\text{Cl}^-$
$\text{Na}_2[\text{CrCl}_5(\text{H}_2\text{O})]$	$2\text{Na}^+ + [\text{CrCl}_5(\text{H}_2\text{O})]^{2-}$

15. (a) Compressibility factor (Z) = $\frac{pV}{RT}$

From van der Waals' equation for 1 mole,

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$



At high pressure, $p \gg \frac{a}{V^2}$, so, $\frac{a}{V^2}$ can be neglected with respect to p .

$$\begin{aligned} \therefore \quad p + \frac{a}{V^2} &= p \\ p(V - b) &= RT \\ \text{or} \quad pV - pb &= RT \\ \text{or} \quad pV &= RT + pb \\ \text{or} \quad \frac{pV}{RT} &= \frac{RT}{RT} + \frac{pb}{RT} \\ \text{or} \quad Z &= 1 + \frac{pb}{RT} \end{aligned}$$

16. (a) $\Delta G = \Delta H - T \cdot \Delta S$

When both ΔH and ΔS are positive, at high temperature, ΔG may be negative or reaction becomes spontaneous.

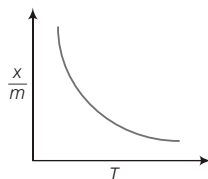
17. (a) London proposed that temporary fluctuations in the electron distributions within atoms could result in the formation of short-lived instantaneous dipole moments.

In larger atoms such as Xe, the outer electrons are much less strongly attracted to the nucleus because of filled inner shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous dipole or induced dipoles. This intermolecular force (instantaneous dipole-induced dipole) is responsible in allowing xenon gas to liquefy.

18. (b) D_2O is used as a moderator to slow down the speed of neutrons in nuclear reactors.

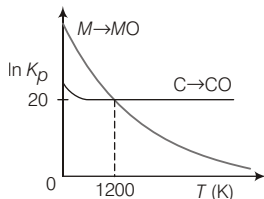
19. (d) Given, adsorption process arises due to van der Waals' forces and it is reversible. Hence, the adsorption is physisorption.

- Enthalpy of physisorption is low (20-35 kJ/mol).
- Physisorption is multilayered.
- Physisorption decreases with increase in temperature.

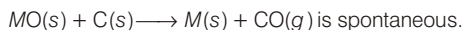


- Physisorption required less activation energy.

20. (d) According to Ellingham diagram,



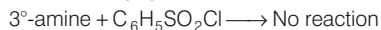
At $T < 1200$ K, carbon will reduce $MO(s)$ to $M(s)$, hence chemical reaction



21. (a)

22. (d) In electrochemical series with respect to reduction potential Cu^{2+} lies below Zn^{2+} . Hence, copper metal could not displace Zn^{2+} from $ZnSO_4$ solution.

23. (b) $C_6H_5SO_2Cl$ is also known as Hinsberg reagent.



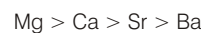
24. (c) For $n = 5$, total number of subshells are

$$5s, 5p, 5d, 5f, 5g$$

\therefore Total number of orbitals

$$= 1 + 3 + 5 + 7 + 9 = 25$$

25. (b) On moving down the group, solubility of sulphates of alkaline earth metals in water decreases. Hence, correct order is



26. (b) 8 g sulphur present in 100 g of organic compound.

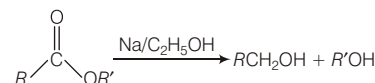
1 g sulphur will present in $\frac{100}{8}$ g of organic compound.

\therefore 32 g sulphur will present in $\left(\frac{100}{8} \times 32\right)$ g of organic compound.

\therefore Minimum molecular weight of the compound

$$= \frac{100}{8} \times 32 = 400 \text{ g mol}^{-1}$$

27. (b) Bouveault-Blanc reduction



Hence, this reaction reduces ester into alcohols.

28. (c) $pI = \frac{pK_1 + pK_p}{2} = \frac{1.88 + 3.65}{2} = 2.77$

29. (b) $H_3AsO_4 \xrightarrow{H_2S/\text{conc. HCl}} As_2S_5$
35.5 g

Assuming 100% conversion of As and applying POAC rule on As atom, we get

$$1 \times \text{Number of moles of } H_3AsO_4 = 2 \times \text{Number of moles of } As_2S_5$$

$$\begin{aligned} \text{Number of moles of } As_2S_5 &= \frac{35.5}{142 \times 2} \\ &= 0.125 \text{ mol} \end{aligned}$$

30. (b) According to Henry's law,

$$\frac{p_1}{p_2} = \frac{s_1}{s_2}$$

[p_1 and p_2 are partial pressures and s_1 and s_2 are solubilities]

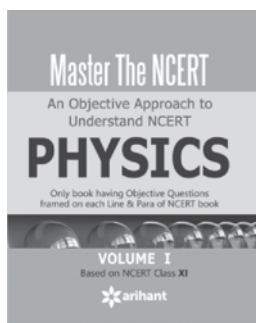
$$\frac{500}{750} = \frac{0.01}{s_2}$$

$$\text{or} \quad s_2 = \frac{750 \times 0.01}{500} = 0.015 \text{ g L}^{-1}$$

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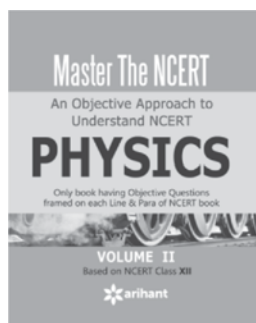
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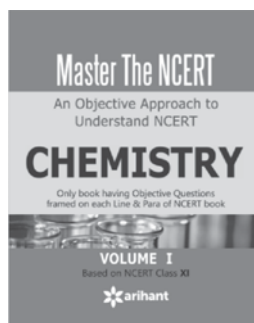
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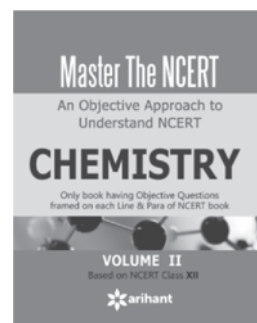
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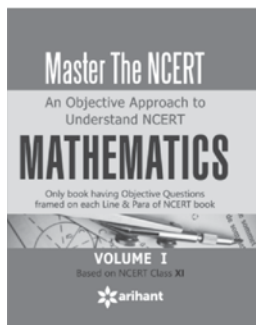
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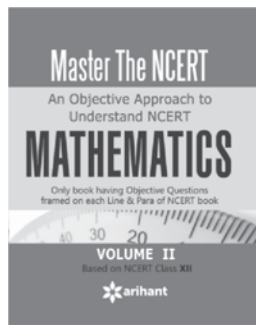
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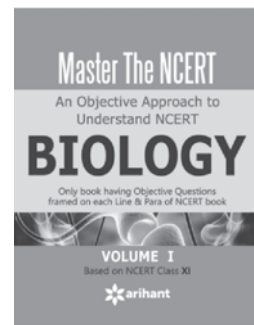
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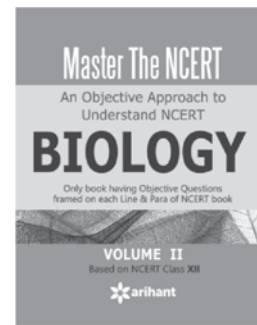
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NEET 2016

NATIONAL ELIGIBILITY CUM ENTRANCE TEST

(PHASE I)

SOLVED PAPER

INSTRUCTIONS

- This test consists of 45 questions and each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 mark will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instruction.

EXAM CRUX

- In chemistry, there are 45 questions asked in NEET entrance exam.
- On an approximation 24 to 26 Questions are asked from class 12th while 19 to 21 are asked from class 11th.
- Except 7 Questions which are numerical based, all other questions are based on theory. In some questions, direct formula has asked. While some questions are related to finding order with respect to different quantities.
- According to topicwise weightage questions asked from class XI are: *Chemical Bonding and Thermodynamics*-4Qs from each, *Some Basic Principles of Organic Chemistry*-4Qs, *States of Matter, Atomic Structure, Equilibrium, Periodic Properties, Hydrogen, s-block Elements, Hydrocarbons*-1Q from each topic.

From Class XII *Biomolecules*-4Qs, *Metallurgy*-3Qs, *Solid State, Solution, Chemical Kinetics, p-block Elements, Amines, Alcohols, Phenols and ethers* - 2Qs from each, *Electrochemistry, Surface Chemistry, d and f-block elements, Coordination Compounds, Polymers, Chemistry is everyday life*-1Q from each topic.

Difficulty level On an approximation by Arihant team around 40% questions may be considered as easy, 30% moderate and 30% are tough. Overall this year paper was little bit tough to solve.

1. The addition of a catalyst during a chemical reaction alters which of the following quantities?

(a) Internal energy	(b) Enthalpy
(c) Activation energy	(d) Entropy

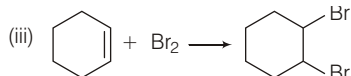
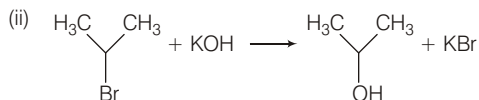
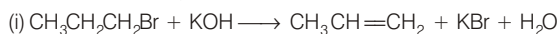
2. Predict the correct order among the following.

(a) Lone pair-lone pair > bond pair-bond pair > lone pair-bond pair
(b) Bond pair-bond pair > lone pair-bond pair > lone pair-lone pair
(c) Lone pair-bond pair > bond pair-bond pair > lone pair-lone pair
(d) Lone pair-lone pair > lone pair-bond pair > bond pair-bond pair
3. The correct statement regarding the basicity of arylamines is

(a) Arylamines are generally more basic than alkylamines because the nitrogen lone-pair electrons are not delocalised by interaction with the aromatic ring π -electron system
(b) Arylamines are generally more basic than alkylamines because of aryl group
(c) Arylamines are generally more basic than alkylamines because the nitrogen atom in arylamines is sp -hybridised
(d) Arylamines are generally less basic than alkylamines because the nitrogen lone-pair electrons are delocalised by interaction with the aromatic ring π -electron system.
4. When copper is heated with conc. HNO_3 , it produces

(a) $\text{Cu}(\text{NO}_3)_2$ and NO
(b) $\text{Cu}(\text{NO}_3)_2$, NO and NO_2
(c) $\text{Cu}(\text{NO}_3)_2$ and N_2O
(d) $\text{Cu}(\text{NO}_3)_2$ and NO_2

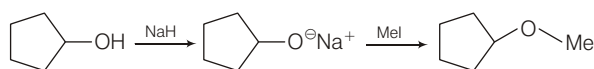
5. For the following reactions,



which of the following statements is correct?

- (a) (i) is elimination reaction, (ii) is substitution and (iii) is addition reaction
 (b) (i) is elimination, (ii) and (iii) are substitution reactions
 (c) (i) is substitution, (ii) and (iii) are addition reactions
 (d) (i) and (ii) are elimination reactions and (iii) is addition reaction
6. Two electrons occupying the same orbital are distinguished by
 (a) magnetic quantum number (b) azimuthal quantum number
 (c) spin quantum number (d) principal quantum number

7. The reaction



can be classified as

- (a) alcohol formation reaction
 (b) dehydration reaction
 (c) Williamson alcohol synthesis reaction
 (d) Williamson ether synthesis reaction
8. The electronic configurations of Eu (Atomic no. 63), Gd (Atomic no. 64) and Tb (Atomic no. 65) are
 (a) $[\text{Xe}] 4f^6 5d^1 6s^2$, $[\text{Xe}] 4f^7 5d^1 6s^2$ and $[\text{Xe}] 4f^9 6s^2$
 (b) $[\text{Xe}] 4f^6 5d^1 6s^2$, $[\text{Xe}] 4f^7 5d^1 6s^2$ and $[\text{Xe}] 4f^8 5d^1 6s^2$
 (c) $[\text{Xe}] 4f^7 6s^2$, $[\text{Xe}] 4f^7 5d^1 6s^2$ and $[\text{Xe}] 4f^9 6s^2$
 (d) $[\text{Xe}] 4f^1 6s^2$, $[\text{Xe}] 4f^8 6s^2$ and $[\text{Xe}] 4f^9 5d^1 6s^2$
9. At 100°C , the vapour pressure of a solution of 6.5 g of a solute in 100 g water is 732 mm. If $K_b = 0.52$, the boiling point of this solution will be
 (a) 100°C (b) 102°C
 (c) 103°C (d) 101°C

10. The correct statement regarding the comparison of staggered and eclipsed conformations of ethane, is

- (a) The eclipsed conformation of ethane is more stable than staggered conformation, because eclipsed conformation has no torsional strain
 (b) The eclipsed conformation of ethane is more stable than staggered conformation even though the eclipsed conformation has torsional strain
 (c) The staggered conformation of ethane is more stable than eclipsed conformation, because staggered conformation has no torsional strain
 (d) The staggered conformation of ethane is less stable than eclipsed conformation, because staggered conformation has torsional strain

11. Which one of the following characteristics is associated with adsorption?

- (a) ΔG , ΔH and ΔS all are negative
 (b) ΔG and ΔH are negative but ΔS is positive
 (c) ΔG and ΔS are negative but ΔH is positive
 (d) ΔG is negative but ΔH and ΔS are positive

12. Match the compounds given in Column I with the hybridisation and shape given in Column II and mark the correct option.

Column I	Column II
A. XeF_6	1. Distorted octahedral
B. XeO_3	2. Square planar
C. XeOF_4	3. Pyramidal
D. XeF_4	4. Square pyramidal

Codes

	A	B	C	D		A	B	C	D
(a)	1	2	4	3	(b)	4	3	1	2
(c)	4	1	2	3	(d)	1	3	4	2

13. The correct statement regarding a carbonyl compound with a hydrogen atom on its alpha-carbon, is

- (a) A carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration
 (b) A carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation
 (c) A carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism
 (d) A carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol

14. In a protein molecule, various amino acids are linked together by

- (a) β -glycosidic bond (b) peptide bond
 (c) dative bond (d) α -glycosidic bond

15. Match items of Column I with the items of Column II and assign the correct code.

Column I	Column II
A. Cyanide process	1. Ultrapure Ge
B. Froth floatation process	2. Dressing of ZnS
C. Electrolytic reduction	3. Extraction of Al
D. Zone refining	4. Extraction of Au
	5. Purification of Ni

Codes

	A	B	C	D		A	B	C	D
(a)	2	3	1	5	(b)	1	2	3	4
(c)	3	4	5	1	(d)	4	2	3	1

16. Which of the following is an analgesic?

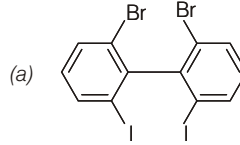
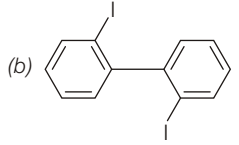
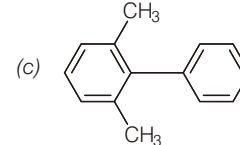
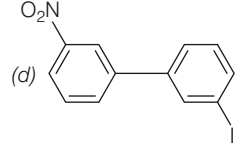
- (a) Penicillin
 (b) Streptomycin
 (c) Chloramycetin
 (d) Novalgin

 EXAM SPECTRUM

- 17.** Which is the correct statement for the given acids?
 (a) Phosphinic acid is a monoprotic acid while phosphonic acid is a diprotic acid
 (b) Phosphinic acid is a diprotic acid while phosphonic acid is a monoprotic acid
 (c) Phosphinic acid and phosphonic acid are triprotic acids
 (d) Phosphinic acid and phosphonic acid are diprotic acids
- 18.** The pair of electron in the given carbanion, $\text{CH}_3\text{C}\equiv\text{C}^-$, is present in which orbitals?
 (a) sp^3 (b) sp^2 (c) sp (d) $2p$
- 19.** Consider the molecules CH_4 , NH_3 and H_2O . Which of the given statements is false?
 (a) The $\text{H}-\text{O}-\text{H}$ bond angle in H_2O is larger than the $\text{H}-\text{C}-\text{H}$ bond angle in CH_4
 (b) The $\text{H}-\text{O}-\text{H}$ bond angle in H_2O is smaller than the $\text{H}-\text{N}-\text{H}$ bond angle in NH_3
 (c) The $\text{H}-\text{C}-\text{H}$ bond angle in CH_4 is larger than the $\text{H}-\text{N}-\text{H}$ bond angle in NH_3
 (d) The $\text{H}-\text{C}-\text{H}$ bond angle in CH_4 , the $\text{H}-\text{N}-\text{H}$ bond angle in NH_3 and the $\text{H}-\text{O}-\text{H}$ bond angle in H_2O all are greater than 90°
- 20.** Which one of the following statements is correct when SO_2 is passed through acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution?
 (a) The solution is decolourised
 (b) SO_2 is reduced
 (c) Green $\text{Cr}_2(\text{SO}_4)_3$ is formed
 (d) The solution turns blue
- 21.** The correct thermodynamic conditions for the spontaneous reaction at all temperatures is
 (a) $\Delta H > 0$ and $\Delta S < 0$ (b) $\Delta H < 0$ and $\Delta S > 0$
 (c) $\Delta H < 0$ and $\Delta S < 0$ (d) $\Delta H < 0$ and $\Delta S = 0$
- 22.** Natural rubber has
 (a) all *trans*-configuration
 (b) alternate *cis* and *trans*-configuration
 (c) random *cis* and *trans*-configuration
 (d) all *cis*-configuration
- 23.** In which of the following options, the order of arrangement does not agree with the variation of property indicated against it?
 (a) $\text{B} < \text{C} < \text{N} < \text{O}$ (increasing first ionisation enthalpy)
 (b) $\text{I} < \text{Br} < \text{Cl} < \text{F}$ (increasing electron gain enthalpy)
 (c) $\text{Li} < \text{Na} < \text{K} < \text{Rb}$ (increasing metallic radius)
 (d) $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+ < \text{F}^-$ (increasing ionic size)
- 24.** Which of the following reagents would distinguish *cis*-cyclopenta-1, 2-diol from the *trans*-isomer?
 (a) Ozone (b) MnO_2
 (c) Aluminium isopropoxide (d) Acetone
- 25.** The product obtained as a result of a reaction of nitrogen with CaC_2 is
 (a) CaCN (b) CaCN_3
 (c) Ca_2CN (d) CaCN_2
- 26.** Fog is a colloidal solution of
 (a) gas in liquid (b) solid in gas
 (c) gas in gas (d) liquid in gas
- 27.** Which one of the following orders is correct for the bond dissociation enthalpy of halogen molecules?
 (a) $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$ (b) $\text{Br}_2 > \text{I}_2 > \text{F}_2 > \text{Cl}_2$
 (c) $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ (d) $\text{I}_2 > \text{Br}_2 > \text{Cl}_2 > \text{F}_2$
- 28.** Equal moles of hydrogen and oxygen gases are placed in container with a pin-hole through which both can escape. What fraction of the oxygen escapes in the time required for one-half of the hydrogen to escape?
 (a) $1/4$ (b) $3/8$
 (c) $1/2$ (d) $1/8$
- 29.** Lithium has a bcc structure. Its density is 530 kg m^{-3} and its atomic mass is 6.94 g mol^{-1} . Calculate the edge length of a unit cell of lithium metal.
 ($N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$)
 (a) 352 pm (b) 527 pm
 (c) 264 pm (d) 154 pm
- 30.** Which of the following statements about the composition of the vapour over an ideal 1:1 molar mixture of benzene and toluene is correct? Assume that the temperature is constant at 25°C . (Given, vapour pressure data at 25°C , benzene = 12.8 kPa, toluene = 3.85 kPa)
 (a) The vapour will contain a higher percentage of toluene
 (b) The vapour will contain equal amounts of benzene and toluene
 (c) Not enough information is given to make a prediction
 (d) The vapour will contain a higher percentage of benzene
- 31.** Which of the following has longest C—O bond length? (Free C—O bond length in CO is 1.128 \AA .)
 (a) $[\text{Co}(\text{CO})_4]^-$ (b) $[\text{Fe}(\text{CO})_4]^{2-}$
 (c) $[\text{Mn}(\text{CO})_6]^+$ (d) $\text{Ni}(\text{CO})_4$
- 32.** Among the following, the correct order of acidity is
 (a) $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$
 (b) $\text{HClO}_2 < \text{HClO} < \text{HClO}_3 < \text{HClO}_4$
 (c) $\text{HClO}_4 < \text{HClO}_2 < \text{HClO} < \text{HClO}_3$
 (d) $\text{HClO}_3 < \text{HClO}_4 < \text{HClO}_2 < \text{HClO}$
- 33.** In the reaction,

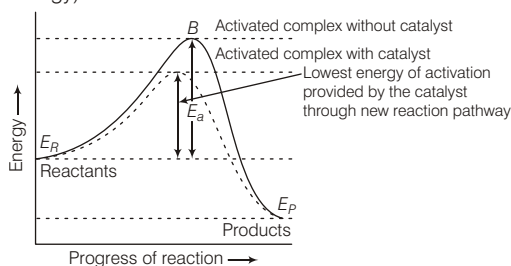
$$\text{H}-\text{C}\equiv\text{CH} \xrightarrow[\text{(ii) CH}_3\text{CH}_2\text{Br}]{\text{(i) NaNH}_2/\text{liq. NH}_3} \text{X} \xrightarrow[\text{(ii) CH}_3\text{CH}_2\text{Br}]{\text{(i) NaNH}_2/\text{liq. NH}_3} \text{Y}$$

 X and Y respectively are
 (a) 2-butyne and 3-hexyne
 (b) 2-butyne and 2-hexyne
 (c) 1-butyne and 2-hexyne
 (d) 1-butyne and 3-hexyne
- 34.** MY and NY_3 , two nearly insoluble salts, have the same K_{sp} values of 6.2×10^{-13} at room temperature. Which statement would be true in regard to MY and NY_3 ?
 (a) The molar solubility of MY in water is less than that of NY_3
 (b) The salts MY and NY_3 are more soluble in 0.5 M KY than that in pure water
 (c) The addition of the salt of KY to solution of MY and NY_3 will have no effect on their solubilities
 (d) The molar solubilities of MY and NY_3 in water are identical

35. Consider the nitration of benzene using mixed conc. H_2SO_4 and HNO_3 . If a large amount of KHSO_4 is added to the mixture, the rate of nitration will be
 (a) slower (b) unchanged
 (c) doubled (d) faster
36. The product formed by the reaction of an aldehyde with a primary amine is
 (a) ketone
 (b) carboxylic acid
 (c) aromatic acid
 (d) Schiff's base
37. The pressure of H_2 required to make the potential of H_2 -electrode zero in pure water at 298 K is
 (a) 10^{-12} atm (b) 10^{-10} atm
 (c) 10^{-4} atm (d) 10^{-14} atm
38. The correct statement regarding RNA and DNA, respectively is
 (a) The sugar component in RNA is ribose and the sugar component in DNA is 2'-deoxyribose
 (b) The sugar component in RNA is arabinose and the sugar component in DNA is ribose
 (c) The sugar component in RNA is 2'-deoxyribose and the sugar component in DNA is arabinose
 (d) The sugar component in RNA is arabinose and the sugar component in DNA is 2'-deoxyribose
39. Which one given below is a non-reducing sugar?
 (a) Lactose (b) Glucose (c) Sucrose (d) Maltose
40. Which of the following statements about hydrogen is incorrect?
 (a) Hydrogen never acts as a cation in ionic salts
 (b) Hydronium ion, H_3O^+ exists freely in solution
 (c) Dihydrogen does not act as a reducing agent
 (d) Hydrogen has three isotopes of which tritium is the most common
41. Consider the following liquid-vapour equilibrium
 Liquid \rightleftharpoons Vapour
 Which of the following relations is correct?
 (a) $\frac{d \ln p}{dT} = \frac{-\Delta H_v}{RT}$ (b) $\frac{d \ln p}{dT^2} = \frac{-\Delta H_v}{T^2}$
 (c) $\frac{d \ln p}{dT} = \frac{-\Delta H_v}{RT^2}$ (d) $\frac{d \ln G}{dT} = \frac{-\Delta H_v}{RT^2}$
42. Which of the following biphenyls is optically active?
 (a)  (b) 
 (c)  (d) 
43. Which of the following statements is false?
 (a) Ca^{2+} ions are important in blood clotting
 (b) Ca^{2+} ions are not important in maintaining the regular beating of the heart
 (c) Mg^{2+} ions are important in the green parts of plants
 (d) Mg^{2+} ions form a complex with ATP
44. The ionic radii of A^+ and B^- ions are 0.98×10^{-10} m and 1.81×10^{-10} m. The coordination number of each ion in AB is
 (a) 4 (b) 8 (c) 2 (d) 6
45. The rate of a first-order reaction is $0.04 \text{ mol L}^{-1} \text{ s}^{-1}$ at 10 s and $0.03 \text{ mol L}^{-1} \text{ s}^{-1}$ at 20 s after initiation of the reaction. The half-life period of the reaction is
 (a) 34.1 s (b) 44.1 s (c) 54.1 s (d) 24.1 s

Answers with Explanation

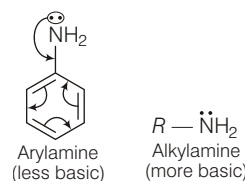
1. (c) A catalyst is a substance which alters the reaction rate but itself remains unchanged in amount and chemical composition at the end of the reaction. It provides a new reaction path with a lower energy barrier (lowering activation energy).



2. (d) According to the postulate of VSEPR theory, a lone pair occupies more space than a bond pair, since it lies closer to the central atom. This means that the repulsion between the different electron pairs follows the order:

$$lp - lp > lp - bp > bp - bp$$

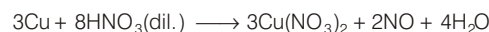
3. (d)



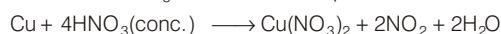
Due to delocalisation of lone pair of electrons of N-atom to the benzene ring, it loses its basicity and becomes less basic than alkyamine.

On the other hand, alkyamine has free lone pair of electron as well as +I-effect of alkyl group that increases electron density on N-atom enhancing its basic nature.

4. (d) Nitric acid acts as an oxidising agent while reacting with copper. When dil. HNO_3 reacts, reaction proceeds as:

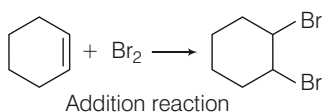
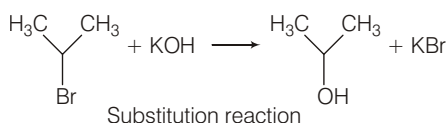


and when conc. HNO_3 is used, reaction proceeds as

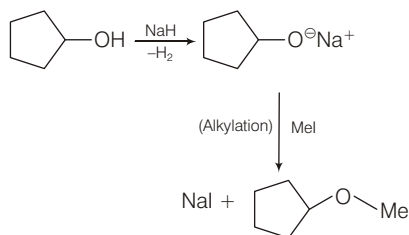


 EXAM SPECTRUM

5. (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{KOH} \longrightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{KBr} + \text{H}_2\text{O}$
Elimination reaction



6. (c) Two electrons occupying the same orbital have equal spin but the directions of their spin are opposite. Hence, spin quantum number, s , (represented by $+1/2$ and $-1/2$) distinguishes them.
7. (d) The formation of ether from alcohol in the presence of base followed by alkylation is known as Williamson ether synthesis reaction.



8. (c) Electronic configuration of ${}_{63}\text{Eu} = [\text{Xe}]_{54} 4f^7 6s^2$
Electronic configuration of ${}_{64}\text{Gd} = [\text{Xe}]_{54} 4f^7 5d^1 6s^2$
Electronic configuration of ${}_{65}\text{Tb} = [\text{Xe}]_{54} 4f^9 6s^2$

9. (d) From Raoult's law of partial pressure,

$$\frac{p_A^\circ - p_s}{p_s} = \frac{n_B}{n_A}$$

$$\Rightarrow \frac{760 - 732}{732} = \frac{W_B \times M_A}{M_B \times W_A}$$

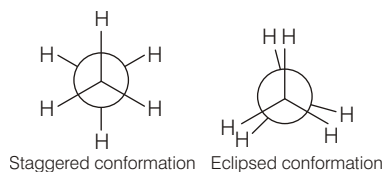
$$\Rightarrow \frac{28}{732} = \frac{6.5 \times 18}{M_B \times 100}$$

$$\Rightarrow M_B = 30.6$$

$$\therefore \Delta T_b = 0.52 \times \frac{6.5 \times 1000}{30.6 \times 100} = 1.10$$

$$\therefore \text{Boiling point} = 100 + 1.10 = 101.1^\circ\text{C} \approx 101^\circ\text{C}$$

10. (c) Due to the absence of torsional strain, staggered conformation of ethane is more stable than eclipsed conformation of it.



11. (a) Adsorption is a spontaneous process that occurs with release in energy and decrease in the randomness (i.e. entropy) of the adsorbed substance.

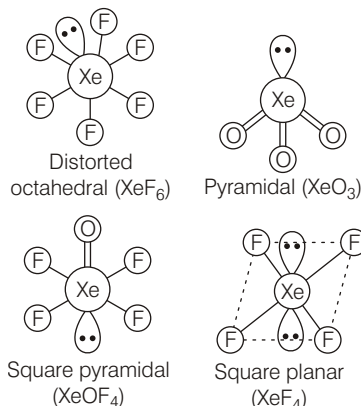
For a spontaneous process, ΔG must be negative.

$$\Delta G = \Delta H - T\Delta S$$

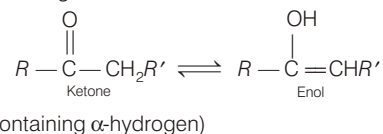
As the process is exothermic and randomness of molecule (entropy) decreases hence, both ΔH and ΔS will be negative as well.

12. (d) A - 1, B - 3, C - 4, D - 2

The structure of the xenon compounds are represented below:

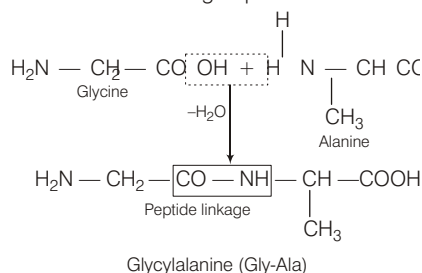


13. (c) In keto-enol tautomerism, a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol.



14. (b) Two amino acids in a protein are linked by a peptide bond.

e.g. glycylalanine is formed when carboxyl group of glycine combines with the amino group of alanine.



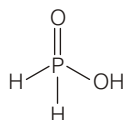
15. (d) A - 4, B - 2, C - 3, D - 1

- **Cyanide process** It is a metallurgical technique for extracting Au (gold) from low grade ore by converting Au to a water-soluble coordination complex.
- **Froth floatation process** This process is used for dressing of sulphide ore, i.e. ZnS .
- **Electrolytic reduction** This process is used for extraction of Al which is carried out in a steel tank lined inside with graphite. Here, graphite serves as a cathode. The electrolyte consists of alumina dissolved in fused cryolite (Na_3AlF_6) and fluorspar (CaF_2).

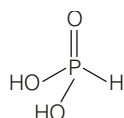
- **Zone refining** This process is used for ultrapure Ge element. An ingot of Ge is first purified by zone refining. Then a small amount of antimony is placed in the molten zone which is passed through the pure Ge with the proper choice of rate of heating and other variables.

16. (d) Novalgin (Dipyron) is a non-narcotic analgesic used as pain reliever.
Penicillin is an antibiotic used for curing rheumatic fever.
Streptomycin is an antibiotic drug.
Chloromycetin is an antibiotic drug.

17. (a) Phosphinic acid



Phosphinic acid



Due to the presence of one replaceable proton in phosphinic acid, it is monoprotic acid. And due to presence of two replaceable protons in phosphonic acid, it is diprotic acid.

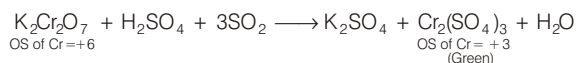
18. (c) Hybridisation = $\frac{\text{Number of } \sigma \text{ - electrons}}{2}$
 $= \frac{2 + 2 (\text{negative ion})}{2} = 2 = sp$

Hence, in the carbanion, $\text{CH}_3\text{C}\equiv\text{C}^-$, pair of electron as negative charge is present in sp -hybridised orbital.

19. (a) As the number of lone pair of electrons on central element increases, repulsion between lone pair of electrons increases and therefore, bond angle decreases.

Molecules	Bond angle
CH_4 (no lone pair of electrons)	109.5°
NH_3 (one lone pair of electrons)	107.5°
H_2O (two lone pair of electrons)	104.45°

20. (c) When SO_2 is passed through acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution, green chromium sulphate is formed. In this reaction, oxidation state of Cr changes from +6 to +3.



The appearance of green colour is due to the reduction of chromium metal.

21. (b,d) We have the Gibbs Helmholtz reaction for spontaneity as $\Delta G = \Delta H - T\Delta S$

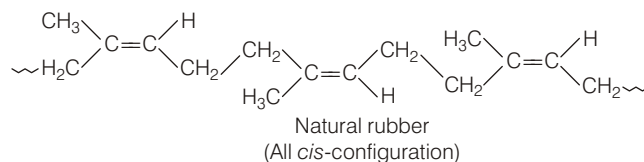
For reaction to be spontaneous, ΔG must be negative.

For this, ΔH should be negative and ΔS should be positive.

$$\therefore \Delta H < 0 \text{ and } \Delta S > 0$$

and also $\Delta S = 0$ shows ΔG is a negative quantity.

22. (d) The repeating unit in natural rubber has the *cis*-configurations with chain extensions on the same side of the ethylene double bond, which is essential for elasticity. If the configuration is *trans*, the polymer is either a hard plastic or a substance like *gutta-percha*.



23. (a,b)

For option (a),

First ionisation energy is the energy required to remove an electron from outermost shell.

Hence, correct order is $\text{B} < \text{C} < \text{O} < \text{N}$.

For option (b),

Electron gain enthalpy is the energy required to gain an electron in the outermost shell.

Hence, the correct order is $\text{I} < \text{Br} < \text{F} < \text{Cl}$.

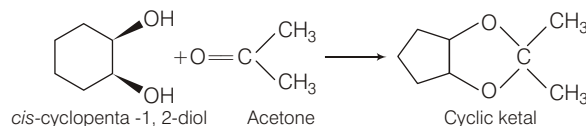
For option (c),

As we move down the group in alkali metals, metallic radius increases as $\text{Li} < \text{Na} < \text{K} < \text{Rb}$.

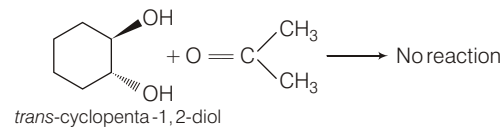
For option (d),

In case of isoelectronic species, as positive charge decreases or negative charge increases the ionic size of the species increases and *vice-versa*, $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+ < \text{F}^-$.

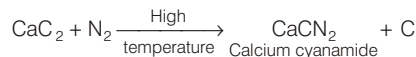
24. (d) *cis*-cyclopenta-1, 2-diol when reacts with acetone, forms cyclic ketal whereas *trans*-isomer of cyclopenta-1, 2-diol cannot form cyclic ketal.



But,



25. (d) When calcium carbide (CaC_2) reacts with nitrogen (N_2) under high temperature, it forms calcium cyanamide which is also called nitrolim.



26. (d) Fog is a colloidal solution of liquid in gas, in which liquid is the dispersed phase whereas gas is the dispersion medium. Examples of other options are as follows:

Gas in liquid Shaving cream, soda water, froth

Solid in gas Dust in air

Gas in gas Atmospheric air

27. (a) As the size increases, bond dissociation enthalpy becomes lower. Also, as the size of atoms get smaller, ion pairs on the two atoms get close enough together to experience repulsion. In case of F_2 , this repulsion is bigger and bond becomes weaker.

Hence, the correct order is $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$.

EXAM SPECTRUM

28. (d) Given, number of moles of hydrogen (n_{H_2}) and that of oxygen (n_{O_2}) are equal.

∴ We have, the relation between ratio of number of moles escaped and ratio of molecular mass.

$$\frac{n_{O_2}}{n_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{O_2}}}$$

where, M = Molecular mass of the molecule

$$\Rightarrow \frac{n_{O_2}}{n_{H_2}} = \sqrt{\frac{2}{32}} \Rightarrow \frac{n_{O_2}}{n_{H_2}} = \sqrt{\frac{1}{16}}$$

$$\Rightarrow \frac{n_{O_2}}{0.5} = \frac{1}{4} \Rightarrow n_{O_2} = \frac{0.5}{4} = \frac{1}{8}$$

29. (a) Given, Li has a bcc structure.

Density (ρ) = 530 kgm⁻³

Atomic mass (M) = 6.94 g mol⁻¹

Avogadro's number (N_A) = 6.02 × 10²³ mol⁻¹

We know that, number of atoms per unit cell in bcc (Z) = 2.

∴ We have the formula for density,

$$\rho = \frac{ZM}{N_A a^3}$$

where, a = edge length of a unit cell

$$\text{or } a = \sqrt[3]{\frac{ZM}{\rho N_A}} = \sqrt[3]{\frac{2 \times 6.94 \text{ g mol}^{-1}}{0.53 \text{ g cm}^{-3} \times 6.02 \times 10^{23} \text{ mol}^{-1}}}$$

$$= \sqrt[3]{4.35 \times 10^{-23} \text{ cm}^{-3}} = 3.52 \times 10^{-8} \text{ cm}$$

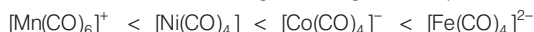
$$a = 352 \text{ pm}$$

30. (d) Since, component having higher vapour pressure will have higher percentage in vapour phase. Benzene has vapour pressure 12.8 kPa which is greater than of toluene 3.85 kPa. Therefore, the vapour will contain a higher percentage of benzene.

31. (b) As negative charge on metal carbonyl complex increases, back π -bonding increases and hence, bond length of C—O bond increases while bond length of metal-carbon bond decreases.

Hence, $[\text{Fe}(\text{CO})_4]^{2-}$ has longest C—O bond length among the given complexes.

The correct order of bond length of the given complexes is



32. (a) As the oxidation state of halogen, i.e. —Cl in this case increases, acidity of oxyacid increases.

HClO : Oxidation state of Cl = + 1

HClO₂ : Oxidation state of Cl = + 3

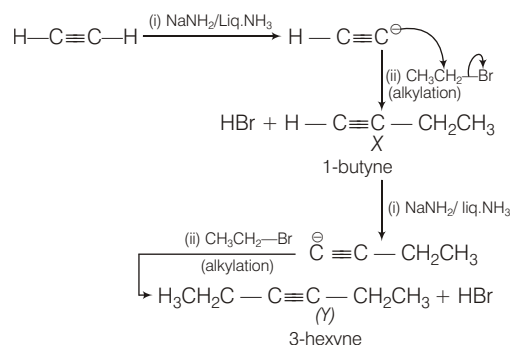
HClO₃ : Oxidation state of Cl = + 5

HClO₄ : Oxidation state of Cl = + 7

Therefore, the correct order of acidity would be



33. (d) Since, $\text{NaNH}_2/\text{liq.NH}_3$ behaves as a base, so it abstracts proton from acetylene to form acetylide anion followed by alkylation to give compound (X), i.e. 1-butyne. X further reacts with $\text{NaNH}_2/\text{liq.NH}_3$ followed by alkylation with ethyl bromide yields 3-hexyne (Y).



34. (a) For MY , $MY \rightleftharpoons M^+_s + Y^-_s$

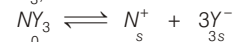
where, s = solubility and K_{sp} = solubility product

$$\therefore K_{sp} = [M^+] [Y^-]$$

$$K_{sp} = s^2$$

$$s = \sqrt{K_{sp}} = \sqrt{6.2 \times 10^{-13}} = 7.874 \times 10^{-7}$$

Similarly, for NY_3 ,



$$\therefore K_{sp} = [N^+] [Y^-]^3 = s \times (3s)^3$$

$$K_{sp} = 27s^4$$

$$\therefore s = \sqrt[4]{\frac{K_{sp}}{27}} = \sqrt[4]{\frac{6.2 \times 10^{-13}}{27}} = 3.89 \times 10^{-4}$$

Therefore, molar solubility of MY in water is less than that of NY_3 .

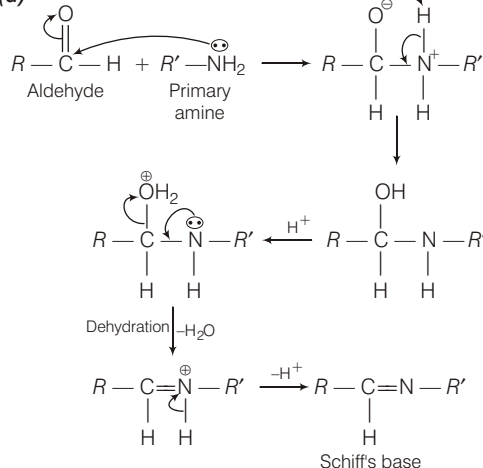
35. (a) In the nitration of benzene in the presence of conc. H_2SO_4 and HNO_3 , nitrobenzene is formed.



If large amount of KHSO_4 is added to this mixture, more HSO_4^- ion furnishes and hence, the concentration of NO_2^+ , i.e. electrophile decreases.

As concentration of electrophile decreases, rate of electrophilic aromatic reaction slows down.

36. (d)



37. (d) From the question, we have an equation



According to Nernst equation,

$$E = E^\circ - \frac{0.0591}{n} \log \frac{p_{\text{H}_2}}{[\text{H}^+]^2}$$

$$= 0 - \frac{0.0591}{2} \log \frac{p_{\text{H}_2}}{(10^{-7})^2} \quad [\because [\text{H}^+] = 10^{-7}]$$

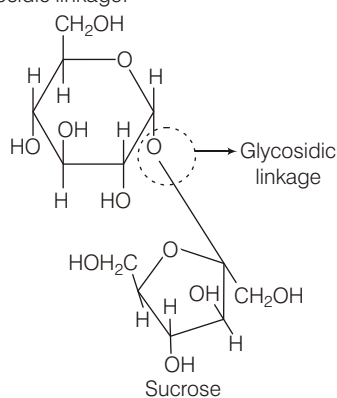
\therefore For potential of H_2 electrode to be zero, p_{H_2} should be equal to $[\text{H}^+]^2$, i.e. 10^{-14} atm.

$$\therefore \log \frac{10^{-14}}{(10^{-7})^2} = 0$$

- 38. (a)** In DNA, two helically twisted strands connected together by steps. Each strand consists of alternating molecules of deoxyribose at 2'-position and phosphate groups. On the other hand, in RNA, the pentose sugar has an identical structure with deoxyribose sugar except that there is an $-\text{OH}$ group instead of $-\text{H}$ on 2' carbon atom. Hence, it is only called ribose.

- 39. (c)** Sucrose is non-reducing sugar because reducing part

of glucose ($-\text{C}-\text{H}$) and fructose ($\text{>C}=\text{O}$) are involved in glycosidic linkage.



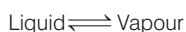
While, lactose, glucose and maltose are reducing sugars.

- 40. (c,d)**

- For ionic salts, hydrogen never behaves as a cation, but behaves as an anion (H^-).
- H_3O^+ exists freely in solution.
- Dihydrogen acts as a reducing agent.
- Hydrogen has three isotopes.
 - Protium (${}^1_1\text{H}$)
 - Deuterium (${}^2_1\text{H}$)
 - Tritium (${}^3_1\text{H}$)

Protium is the most common isotopes of hydrogen with an abundance of 99.98%.

- 41. (c)** The given phase equilibrium is

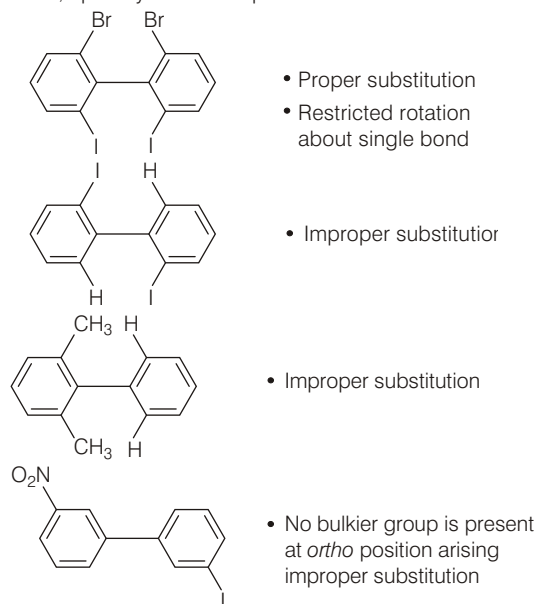


This equilibrium states that, when liquid is heated, it converts into vapour but on cooling, it further converts into liquid, which is derived by Clausius-Clapeyron and the relationship is written as,

$$\frac{d \ln p}{dT} = - \frac{\Delta H_v}{RT^2}$$

where, ΔH_v = Heat of vaporisation

- 42. (a)** The biphenyl compounds having proper substitution at *ortho*-position of benzene ring resulting steric hindrance. This steric hindrance makes the biphenyl system non-planar and hence, optically active compounds.



- 43. (b)** Ca^{2+} ions are very important factor in blood clotting. Ca^{2+} ions are very important for maintaining the regular heart beating.

Mg^{2+} ions are present in the green parts of plants, i.e. chlorophyll.

Mg^{2+} can form a complex with ATP.

- 44. (d)** Given, ionic radius of cation (A^+) = 0.98×10^{-10} m

Ionic radius of anion (B^-) = 1.81×10^{-10} m

\therefore Coordination number of each ion in $AB = ?$

Now, we have

$$\text{Radius ratio} = \frac{\text{Radius of cation}}{\text{Radius of anion}} = \frac{0.98 \times 10^{-10} \text{ m}}{1.81 \times 10^{-10} \text{ m}} = 0.541$$

If radius ratio range is in between 0.441- 0.732, ion would have octahedral structure with coordination number 'six'.

- 45. (d)** Given, order of reaction = 1

Rate of reaction at 10 s = $0.04 \text{ mol L}^{-1} \text{ s}^{-1}$

Rate of reaction at 20 s = $0.03 \text{ mol L}^{-1} \text{ s}^{-1}$

\therefore Half-life period ($t_{1/2}$) = ?

We have the equation of rate-constant 'k' for first order reaction,

$$k = \frac{2.303}{t} \log \frac{[A_t]}{[A_0]} = \frac{2.303}{10} \log \frac{0.04}{0.03} = \frac{2.303}{10} \times 0.124$$

$$k = 0.028 \text{ s}^{-1}$$

We know that,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0287 \text{ s}^{-1}}$$

$$= 24.14 \text{ s} \approx 24.1 \text{ s}$$

PERMANENT ELECTRONIC DISPLACEMENTS IN ORGANIC MOLECULES

Coverage of Special topics for JEE Advanced

Organic molecules are covalent in nature and in most of the cases show non-polar covalent nature because of the presence of C and H atoms (which have narrow differences in their E_N) in them.

Presence of atoms like O, N, S, P and halogens, on the other hand, are responsible for the development of polar characteristics in them. These polarity related characteristics are developed as the result of permanent electronic displacements in organic molecules.

This particular article will give you an insight of the fact that how, why and when these electronic displacements affect organic molecules and their reactivity or stability.

There are four types of electronic displacements found in organic compounds :

- Inductive effect
- Resonance effect
- Hyperconjugation effect
- Electromeric effect

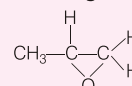
Out of above effects, only electromeric effect is a temporary effect, all others are permanent effects. We shall discuss permanent electronic displacements in this article.

Teachers's NOTE

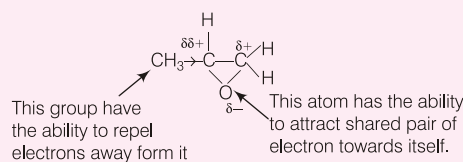
The visualisation of an organic molecule after electronic displacement is very important. It specially helps in understanding the working (mechanism) of organic reactions. Infact through these displacements one can predict.

- The nature of organic molecule, i.e. either polar or non-polar
- The nature or types of all possible reactions which an organic molecule can undergo
- The site of reagent attack

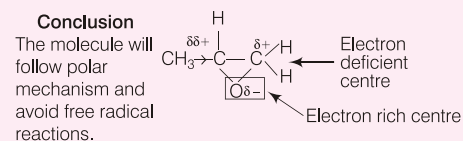
- (d) The possible product formation etc.
e.g. Observe the following molecule



Due to the presence of highly electronegative oxygen atom in it, the electronic distribution of this molecule will be looks like:



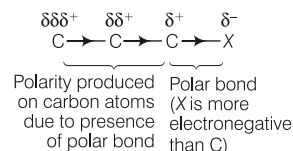
Thus, the molecule have well defined electron rich and electron deficient centres, i.e.



Likewise you can also analyse organic molecules after carefully going through the effects written below.

(a) Inductive Effect

It is defined as the permanent effect whereby polarity is induced on the carbon atom and the substituent attached to it due to minor displacement of bonding electron pairs. This displacement is caused due to their different electronegativities.



Characteristics of Inductive Effect

- It is a permanent effect.
- It operates through σ -bonds.
- Its magnitude decreases as we move away because of polarity (i.e. polar bond).
- It is generally observed in saturated compounds.

Note For practical purpose, the inductive effect is ignored after the second carbon atom. It should be in your mind that the electron pairs although permanently displaced but they do not leave their valence shells.

Types of Inductive Effect

+I-effect (Electron releasing effect)	-I-effect (Electron withdrawing effect)
The atom or group having smaller electron affinity than hydrogen is said to have +I-effect.	The atom or group having greater electron affinity than hydrogen is said to have -I-effect.
This effect produces negative charge on the carbon chain, i.e. increases electron density due to less withdrawing power.	This effect produces positive charge on the carbon chain, i.e. decreases electron density due to more electron withdrawing power.
+I-effect order for some groups follows the order: (CH ₃) ₃ C > (CH ₃) ₂ CH > CH ₃ CH ₂ > CH ₃	-I-effect order for some groups follows the order: —NO ₂ > —F > —COOH > —Cl > —Br > —I > —OH > —C ₆ H ₅

Applications of Inductive Effect

(i) In Determining Dipole Moment

Example 1 Find the decreasing order of dipole moment for compounds, CH₃F, CH₃Cl, CH₃Br and CH₃I.

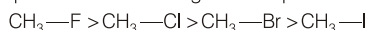
- (a) CH₃I > CH₃Br > CH₃Cl > CH₃F
 (b) CH₃I > CH₃Cl > CH₃Br > CH₃F
 (c) CH₃F > CH₃Cl > CH₃Br > CH₃I
 (d) CH₃F > CH₃Br > CH₃Cl > CH₃I

Sol. (c) As inductive effect leads to a dipolar character within a molecule therefore, greater the inductive effect, more will be dipole moment of the molecule.

Since, -I-effect order of the attached group to the carbon chain is



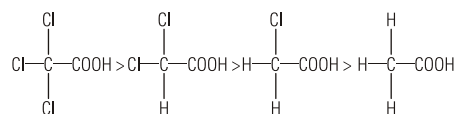
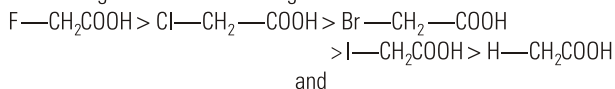
Hence, dipole moment of the given compounds is in the order



Analysis of acidic and basic strengths of carboxylic acids and amines respectively via inductive effect

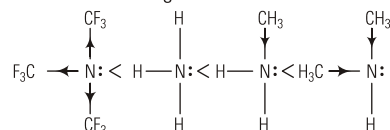
- Acidity of carboxylic acid is due to the ease with which it ionises to give proton and this ease increases with the strength of group showing -I-effect attached to the α -carbon of carboxylic acid or increasing number of groups showing -I-effect.

Decreasing order of acidic strength



- Amines are basic because they are electron pair donors or they can accept protons. Relative basic strength of amines depends upon inductive effect, steric effect and stabilisation of cation by hydration. We will discuss only I-effect here.

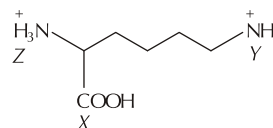
Increasing order of basic strength



More the number of electron donating groups attached to nitrogen atom, more will be its basic strength as electron donating group increases the electron density on N-atom.

(ii) In Determining Acidic Strength

Example 2

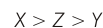


Arrange X, Y and Z in order of decreasing acidic strength.

[IIT JEE 2004]

- (a) X > Z > Y (b) Z < X > Y
 (c) X > Y > Z (d) Z > X > Y

Sol. (a) Carboxylic acid is stronger acid than ammonium ion, hence —COOH(X) is most acidic. —NH₃(Z) is more acidic than —NH₃(Y) due to -I-effect of —COOH on Z. Hence, overall acidic strength order is



Example 3

Match the following with their K_a values.

Benzoic acid	4.2 × 10 ⁻⁵
p-nitrobenzoic acid	3.3 × 10 ⁻⁵
p-chlorobenzoic acid	6.4 × 10 ⁻⁵
p-methyl benzoic acid	36.2 × 10 ⁻⁵
p-methoxy benzoic acid	10.2 × 10 ⁻⁵

[JEE Adv. 2003]

Sol. p-methoxy benzoic acid is the weakest and p-nitrobenzoic acid is the strongest acid among these acids. Chloro group has overall electron withdrawing effect on ring, therefore, increases acidic strength of benzoic acid while methyl group decreases acidic strength of benzoic acid by +I-effect.

Therefore,

Compound	K _a value
p-methoxy benzoic acid	3.3 × 10 ⁻⁵
p-methyl benzoic acid	4.2 × 10 ⁻⁵
Benzoic acid	6.4 × 10 ⁻⁵
p-chlorobenzoic acid	10.2 × 10 ⁻⁵
p-nitrobenzoic acid	36.2 × 10 ⁻⁵

METICULOUS ANALYSIS

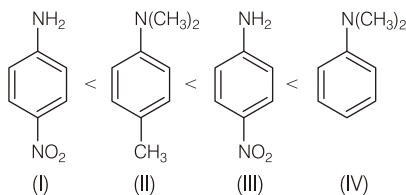
(iii) In Determining Basic Strength

Example 4 Arrange the following in the order of their increasing basicity.

- I. *p*-toluidine II. *N,N*-dimethyl-*p*-toluidine
 III. *p*-nitroaniline IV. Aniline

- (a) III < IV < II < I (b) IV < III < I < II
 (c) III < I < IV < II (d) III < IV < I < II

Sol. (d)



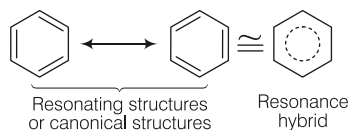
- $-I$ -effect (electron withdrawing) of $-\text{NO}_2$ group decreases the electron density on N of amine group which results decrease in basic strength.
- Due to $+I$ -effect (electron donating) of methyl group, it increases electron density on nitrogen atom of $-\text{NH}_2$ group which results increase in basic strength.
- More the number of methyl groups, more will be the basicity.

(b) Resonance Effect

When several structures may be assumed to contribute to the true structure of the molecule but none of them can be said to represent it uniquely, the molecule is referred to as a resonance hybrid and the phenomenon is termed as **resonance**.

Such several structures are called canonical forms or resonating structures.

e.g.



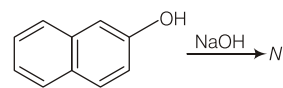
Conditions of Resonance

- The arrangement of atoms must be identical or almost same in each structure of molecule.
- The energy content of all the canonical forms must be same.
- Each canonical form must have the same number of unpaired electrons.

Positive (+R) and Negative (-R) Resonance Effects

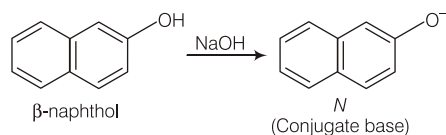
- $+R$ and $-R$ effects are shown by the substituents or groups that donate and gain electrons respectively.
- The electron density on rest of the molecular entity is increased and decreased due to $-R$ and $+R$ -effects.
- Groups showing $+R$ -effects :
 $-\text{OH}$, $-\text{OR}$, $-\text{SH}$, $-\text{SR}$, $-\text{NH}_2$, $-\text{NR}_2$ etc.
- Groups showing $-R$ -effect : $-\text{NO}_2$, carbonyl $>(\text{C}=\text{O})$, $-\text{C}\equiv\text{N}$, $-\text{COOH}$, $-\text{SO}_3\text{H}$ etc.

Example 5 The number of resonance structures for *N* is

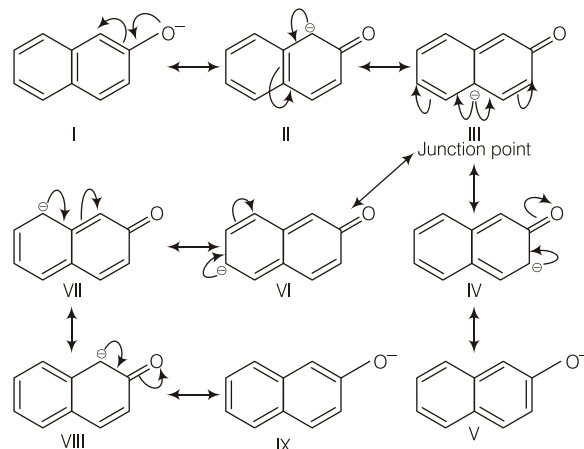


[JEE Advanced 2015]

Sol. (9) Due to the presence of a strong base such as NaOH, β -naphthol loses its proton to form a conjugate base (*N*) which is resonance stabilised.



The resonating structures of *N* are



Therefore, product *N* has nine resonating structures.

Quantities Affected by Resonance

- **Heat of formation** The heat of formation of resonance hybrid is abnormally high.
 e.g. The observed heat of formation of CO_2 ($= 1590 \text{ kJ mol}^{-1}$) is greater than the calculated heat of formation ($= 1464 \text{ kJ mol}^{-1}$) of its most stable structure. It is due to resonance energy which is given as:
 $\therefore \text{Resonance energy} = \text{Heat of formation (Observed)} - \text{Heat of formation (Calculated)}$

Resonance energy is the energy lost when a molecule acquires resonance hybrid formula.

- **Bond length** The bond length in resonance hybrid is variable as compared to bond length in canonical structures.
- **Bond order** The bond order of resonance hybrid is always less than the bond order of its canonical forms.

$$\text{Bond order} = \frac{\text{Total number of bonds between two atoms}}{\text{Total number of resonating structures}}$$

Teachers's NOTE

Before going further into the application of resonance keep following things in mind, i.e.

The concept of resonance is completely **HYPOTHETICAL** means **CANONICAL** or **RESONATING** forms does not have any physical existence.

It is only the so called **Resonance Hybrid** only which has physical existence. This is basically the real structure of organic molecule from the Realistic point of view the concept has its value only because some compounds have partial bonds and these partial bonds are not properly defined anywhere in Chemistry.

Like wise **Resonance energy** also does not have any physical significance. It is a simple difference between the heat of formation of hypothetical and real structure.

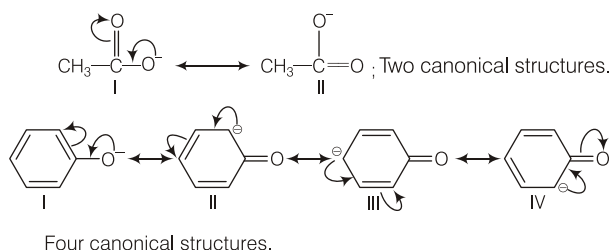
Applications of Resonance

(i) In Determining the Acidic Strength

Example 6 Although, phenoxide ion has more number of resonating structures than acetate ion, benzoic acid is a stronger acid than phenol because

- in case of acetate ion, both the resonance structures are equivalent and negative charge always remains on electronegative oxygen
- in phenoxide ion, negative charge also moves on carbon atoms of benzene ring
- Both (a) and (b)
- None of them

Sol. (c) The factors mentioned in options (a) and (b) are the reason for more acidic nature of benzoic acid than phenoxide ion.



Example 7 Phenol is less acidic than

- acetic acid
- p*-methoxy phenol
- p*-nitrophenol
- ethanol

Sol. (a,c) Phenol is less acidic than carboxylic acid (acetic acid). Nitro group from *para* position exerts electron withdrawing resonance effect, increases acidic strength. Therefore, phenol is less acidic than *p*-nitrophenol.

Methoxy group from *para*-position donates electrons by resonance effect, decreases acidic strength of phenol. Also, ethanol is a weaker acid than phenol due to resonance stabilisation in phenoxide ion. Hence, increasing order of acidic strength will be.

ethanol < *p*-methoxy phenol < phenol < *p*-nitrophenol < acetic acid

Inductive Effect versus Resonance Effect

In most of the cases, resonance effect is stronger and outweighs inductive effect.

e.g. The —OH, —NH₂, —Cl, —Br or —F groups withdraw electrons by *-I*-effect. However, they also release electrons by delocalisation of lone pairs (+*R*-effect).

Since, the resonance effect is more stronger than inductive effect, the net result is electron releasing to rest of the molecule.

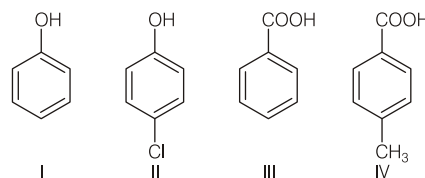
This is clearly observed in phenol and aniline, which are more reactive than benzene towards electrophilic substitution reactions.

Whereas, the inductive effect is stronger than the resonance effect in case of halogen atoms. These are electronegative and hence, exhibit *-I*-effect. However, at the same time, they also release electrons by delocalisation (+*R*-effect) of lone pairs.

This is evident in case of reactivity of halobenzenes, which are less reactive towards electrophilic substitution due to *-I*-effect of halogens.

Example 8 The correct acidity order of the following is

[IIT JEE 2009]



(a) III > IV > II > I

(b) IV > III > I > II

(c) III > II > I > IV

(d) II > III > IV > I

Sol. (a) In structure III, carbonyl group of acid (—COOH) withdraws electrons from the ring. Hence, benzene ring behaves as an electron pair donor species which results maximum acidity of benzoic acid.

In structure IV, methyl group decreases the electron withdrawing nature of carbonyl group of acid as it behaves as electron donating group. Hence, IV is less acidic than III. In structure II, electron withdrawing nature (*-I* effect) of —Cl group dominates over electron donating nature (+*R*) of —Cl. Hence, II is more acidic than I.

In structure I, phenol acquires resonance stabilisation after losing a proton.

Hence, the correct order of acidity is III > IV > II > I.

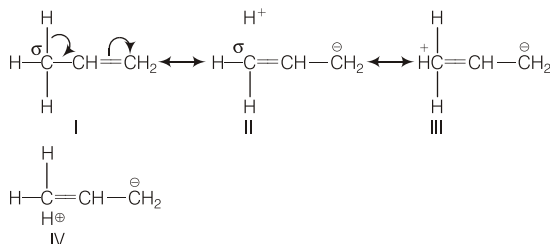
(c) Hyperconjugation

- It is shown by heat of hydrogenation data. It explains that alkenes are stabilised not only by conjugation but also by the presence of alkyl groups. Greater the number of alkyl groups attached to the doubly bonded carbon atoms, the more stable is the alkene.

METICULOUS ANALYSIS

- Stabilisation by alkyl group has been attributed to delocalisation of electrons due to overlapping between a π^* -orbital and a σ -orbital of the alkyl group (C—H bond). Such an overlapping is called hyperconjugation.
- This phenomenon is also called as **no bond resonance** or **Baker-Nathan effect**.

e.g. No bond resonance forms of propene are shown as:



Structural Requirements for Hyperconjugation

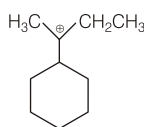
- Compound should have atleast one sp^2 hybridised carbon atom of either alkene, alkyl carbocation or alkyl free radical.
- α -carbon with respect to sp^2 hybrid carbon should have at least one hydrogen. More the number of C—H bonds attached to the unsaturated system, more stable will be the alkene.

Types of Hyperconjugation

(C—H), π -conjugation	(C—H), positive charge conjugation	(C—H), odd electron conjugation
It occurs in alkenes.	It occurs in alkyl carbocations.	It occurs in alkyl free radicals.
e.g. $\text{CH}_3\text{—CH}=\text{CH}_2$, 	$\text{CH}_3\text{—}\overset{+}{\text{C}}\text{H}_2$, $\text{CH}_3\text{—}\overset{+}{\text{C}}(\text{CH}_3)_2$	$\text{CH}_3\text{—}\dot{\text{C}}\text{H}_2$, $\text{CH}_3\text{—}\dot{\text{C}}(\text{CH}_3)_2$

Example 9

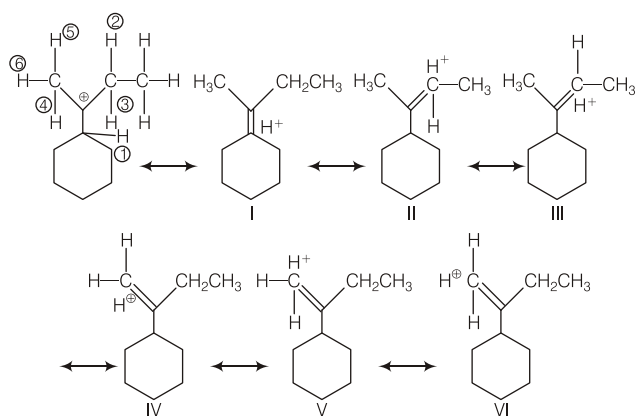
The total number of contributing structures showing hyperconjugation (involving C—H bonds) for the following carbocation is [JEE Adv. 2011]



Sol. (6) Strategy

- First of all, count all the α -hydrogens present at sp^2 hybridised carbon atom.
- Mark all the hydrogen atoms as 1, 2, 3, 4, 5 and 6.
- Draw the hyperconjugative structures one by one with the help of given structure.
- Focus on main structure and replace hydrogen atoms numbered as 1, 2, 3, 4, 5 and 6 and draw their corresponding hyperconjugative structures.

There are total 6 α -hydrogens present at the sp^2 carbon atom. All of these hydrogen atoms participate in hyperconjugation.

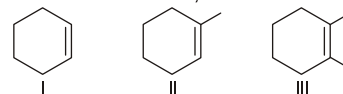


Applications of Hyperconjugation

(i) In Determining the Stability of Alkenes

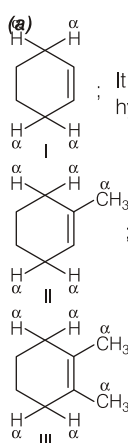
Example 10

The correct stability order of the following is



- (a) III > II > I (b) I > II > III (c) I > III > II (d) III > I > II

Sol.



It has 4 α hydrogens, i.e. will show four hyperconjugative structures.

It has 7 α hydrogens, i.e. will show seven hyperconjugative structures.

It has 10 α hydrogens, i.e. will show ten hyperconjugative structures.

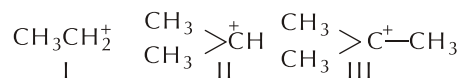
More the number of hyperconjugative structures, more will be the stability.

Hence, order of stability: III > II > I

(ii) In Determining Stability of Alkyl Free Radicals and Carbocations

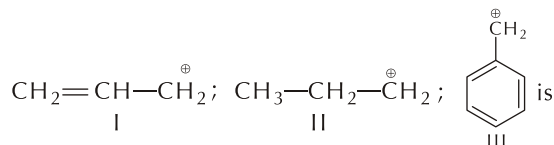
Example 11

The correct order of stability of the following is



- (a) III > II > I
 (b) I > II > III
 (c) III > I > II
 (d) I > III > II

- Sol.** (a) III - 9 α -hydrogens
 II - 6 α -hydrogens
 I - 3 α -hydrogens
 Hence, order of stability is
 III > II > I



[IIT JEE 2013]

Resonance effect vs Hyperconjugation

- Resonance effect involves delocalisation of π -electrons of two or more conjugated double bonds or π -electrons of a double bond and non-bonding electrons of a hetero atom.
- Hyperconjugation is an extension of resonance. It involves delocalisation of σ -electrons through overlapping of p -orbitals of double bond with σ -orbital of adjacent single bond. Hyperconjugation may be regarded as σ - π conjugation.
- Resonance stabilisation dominates over hyperconjugation effect.

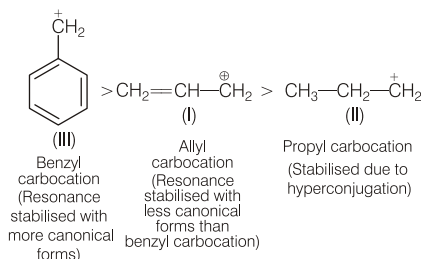
(a) III > II > I

(b) II > III > I

(c) I > II > III

(d) III > I > II

Sol. (d) The order of stability of carbocations will be



Example 12

The order of stability of the following carbocations is

The Basic Books for Aspirants of JEE MAIN & ADVANCED

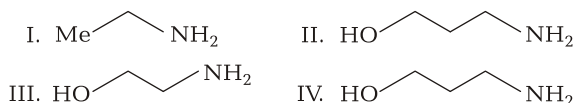
CLASSIC TEXT SERIES

C181	A PROBLEM BOOK IN MATHEMATICAL ANALYSIS	(GN BERMEN)	180/-
C182	PROBLEMS IN MATHEMATICS	(V. GOVOROV, P. DYBOV, N. MIROSHIN, S. SMIRNOVA)	160/-
G437	PROBLEM IN CALCULUS OF ONE VARIABLE	(IA MAROM)	160/-
C264	HIGHER ALGEBRA	(BARNARD & CHILD)	195/-
C048	HIGHER ALGEBRA	(HALL & KNIGHT)	195/-
F042	THE ELEMENTS OF STATICS & DYNAMICS PART 1	(SL LONEY)	115/-
F043	THE ELEMENTS OF STATICS & DYNAMICS PART 2	(SL LONEY)	95/-
C047	THE ELEMENTS OF COORDINATE GEOMETRY PART 1	(SL LONEY)	140/-
C046	PLANE TRIGONOMETRY PART 1	(SL LONEY)	95/-
C260	INTEGRAL CALCULUS FOR BEGINNERS	(JOSEPH EDWARDS)	95/-
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C265	ALGEBRA FOR BEGINNERS	(HS HALL & SR KNIGHT)	130/-
C266	A SCHOOL GEOMETRY	(HS HALL & FH KNIGHT)	120/-
C267	ELEMENTARY ALGEBRA FOR SCHOOLS	(HS HALL & SR KNIGHT)	195/-
C183	PROBLEMS IN GENERAL PHYSICS	(IE IRODOV)	130/-
C261	SCIENCE FOR EVERYONE	(SS KROTOV)	90/-
C259	FUNDAMENTAL LAWS OF MECHANICS	(IE IRODOV)	105/-
C263	BASIC LAWS OF ELECTROMAGNETISM	(IE IRODOV)	125/-

Smart Practice

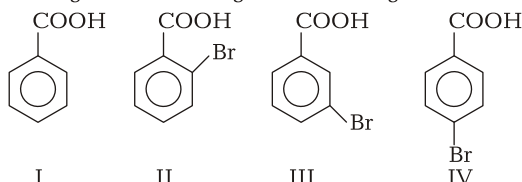
Single Option Correct Type

1. Arrange the following in decreasing order of basicities.



- (a) IV > III > II > I
 (b) I > II > III > IV
 (c) II > III > IV > I
 (d) I > IV > III > II

2. Arrange the following in decreasing order of acidity.



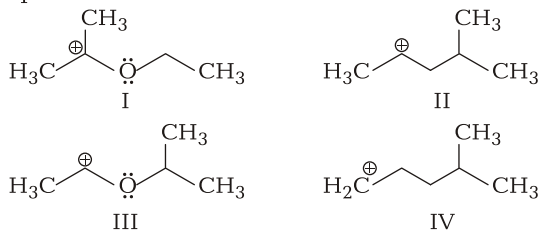
- (a) I > II > III > IV
 (b) III > II > IV > I
 (c) I > III > II > IV
 (d) II > III > IV > I

3. Give the stability order of the following resonance structures.



- (a) I > II > III > IV
 (b) III > II > I < IV
 (c) I > III > II > IV
 (d) III > I > II > IV

4. Give the correct stability order of the following species.



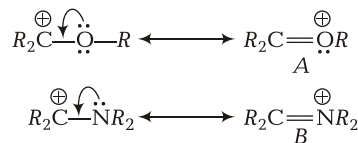
- (a) I > III > II > IV
 (b) I > II > III > IV
 (c) IV > II > III > I
 (d) IV > III > II > I

More than One Option Correct Type

5. Which of the following statements are correct?
 (a) Inductive effect operates through non-bonding electrons of substituent attached to the carbon atom
 (b) The energy content of all the canonical forms of an organic compound showing resonance is same
 (c) Greater the number of alkyl groups attached to the doubly bonded carbon atoms, more stable is the alkene
 (d) All of the above

6. The hyperconjugative stabilities of *tert*-butyl cation and 2-butene, respectively, are not due to
 (a) $\sigma \rightarrow p$ (empty) and $\sigma \rightarrow \pi^*$ electron delocalisations
 (b) $\sigma \rightarrow \sigma^*$ and $p \rightarrow \pi$ electron delocalisations
 (c) $\sigma \rightarrow p$ (filled) and $\sigma-\pi$ electron delocalisations
 (d) p (filled) $\rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ electrons delocalisations

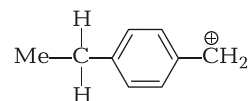
Passage Based Type (Q. Nos. 7-8) The permanent electron displacement causing effects such as resonance, inductive effect or hyperconjugation, delocalise the positive charge of carbocation on total molecule. Hence, these effect increase the stability of carbocation. The atoms with non-bonding electron pairs greatly stabilise carbocations.



7. Which of the above carbocations is comparatively more stable?
 (a) A (b) B
 (c) Both are equally stable (d) None of these
8. The carbocation $CH_2=CH-\overset{\oplus}{C}H_2$ is resonance stabilised whereas the carbocation $CH_2=CHN\overset{\oplus}{Me}_3$ is not. This is because
 (a) the electron donating, $-N\overset{\oplus}{Me}_3$ group can not stabilise the carbocation because of $-I$ -effect
 (b) the nitrogen atom bearing the positive charge has eight valence electrons. It cannot expand its valence electrons to ten. Hence, an alternative resonance structure cannot be drawn
 (c) resonance is more dominating than $-I$ -effect
 (d) All of the above

Integer Type

9. The total number of contributing structures showing hyperconjugation (involving C—H bonds) for the following alkene is



10. The total number of resonating structures of aniline is

Answers

1. (b) 2. (d) 3. (c) 4. (a) 5. (b,c,d) 6. (b,c,d) 7. (b) 8. (b) 9. (3) 10. (5)

Elements : How They were Discovered?

Recently, periodic table has completed its seventh row by the discovery of four new elements having atomic numbers 113, 115, 117 and 118. These elements are among the heaviest in the periodic table and do not exist in nature. They are highly unstable. Day by day, we study about new terms, new compounds formed from their constituent atoms.

Concept of "Chemical Element"

The chemical element is a term denoting atoms having same number of protons in their atomic nuclei (i.e. the same atomic number).

Origin of the Name "Element"

Historians of Chemistry have no consensus in this question. One of the hypotheses explains that the word "element" originates from the letters of the Latin alphabet: *l*, *m*, *n* and *t* which are pronounced as 'el-' 'em'-'en'-'te' (in Latin "elementum"). Probably, pronouncing the word 'element' in this way, the scientists wanted to emphasise that as words are composed of letters, different compounds can be represented as constituted by elements.

How an Element became a Chemical Element?

- Before the modern model of the atom evolved, the concept of an element had been purely speculative.
- Aristotle, one of the greatest philosophers of antiquity wrote that, 'Elements are simple substances of which the universe is composed and one of which cannot be separated into the other'.
- In 16th century, Paracelsus, a famous physician and scientist suggested that all substances consist of three sources: mercury, salt and sulphur, which are the carriers of three qualities : volatility, solidity and inflammability.
- But in 17th century, Robert Boyle, the English chemist, criticised the view of Paracelsus. He said that elements must be material in nature and are constituent solid bodies.
- Antoine Lavoisier's views were a considerable step in this field. He believed that all substances which scientists had failed to decompose in anyway were elements. He also divided simple substances into four groups.

Lavoisier drew no distinction between the concepts of 'an element' and 'a simple body'. They were clearly stated only in the 19th century

owing to the development of the atomic and molecular theory and by the work of DI Mendeleev.

Was there Any Order in Discoveries of Elements?

Naturally, the history of the discovery of chemical elements was affected to an extent by the abundance factor : the elements less abundant in nature were discovered later as these were discovered later.

The history of natural radioactive elements gives a fine illustration of this idea as these were discovered later.

Elements Discovered in Nature

Most chemical elements known at present have been discovered in nature from various ores, minerals and Earth's atmosphere etc. More than 90% of elements occurring in nature are stable, i.e. not radioactive. The number of naturally radioactive elements on earth is considerably smaller than the stable ones.

Elements known in Antiquity

A description of the early history of the elements of antiquity will of necessity have to pass over in silence the dates and the authors of the discoveries.

There are seven metals of antiquity-gold, silver, copper, iron, tin, lead and mercury "the magnification seven" of metals that played a tremendous role in both development of civilisation and various schools of natural philosophy.

Sometime, zinc, platinum, antimony and bismuth are also said to be known in antiquity but there is no definite proof of that.

We shall study one by one about the elements in this topic. From this issue, let's start with sulphur.

Sulphur

- Sulphur has been known to man since ancient times. Even in times of Homer ancient Greeks used the specific properties of sulphur dioxide liberated in the burning of sulphur for disinfection of homes.
- Deposits of native sulphur have also been known from ancient times. Pliny the Elder described that the deposits of sulphur in Italy and Sicily. Sulphur was used for making dyes and treating fabrics in ancient time.
- Sulphur was used in pyrotechnics (a firework display from earliest times known by the name of Greek fire and was invented in the 5th century by Zantium (an ancient Greek colony).

- This mixture contains finely ground sulphur (one part), coal (two parts), and saltpetre (six parts). This mixture differs only slightly from that of black gunpowder.
- In middle ages, sulphur is used as a good combustible material because it readily combines with the great number of metals. This property of sulphur is responsible for its privileged position among substances in the middle ages. Alchemists considered sulphur as the element of combustibility and constituent of all metals.
- Sulphur became recognised as chemical element in 1789, when Antoine Lavoisier included it in his famous list of the elements. However, inspite of the fact that by the beginning of the 19th century, sulphur had already been recognised as an independent element. Experiments had to be carried out to explain the exact composition of native sulphur.
- In 1808, H Davy suggested that sulphur in its usual state is a combination of small amounts of oxygen and hydrogen with a great amount of sulphur. In 1809, Gay Lussac proved it beyond any doubt.
- In 1810, H Davy pointed out that the presence of oxygen in sulphur may be due to sulphur oxides present in native sulphur. The oxygen content in sulphur varied depending on the deposit from where the samples were taken.
- From the standpoint of modern chemistry, one may say that oxygen found by Davy in sulphur, was not oxygen of sulphur oxides but that of oxysulphides of various metals, which are always present in sulphur.
- In 1823, German chemist, Eilhard Mitscherlich discovered allotropes of sulphur. He showed that the crystal shapes of sulphur obtained after cooling molten sulphur was different from those obtained when the element crystallised from a solution. The sulphur obtained from molten sulphur is called monoclinic sulphur, while from crystallising a solution is called rhombic sulphur. Both forms consist of S_8 rings. The difference between the two forms is the way the rings are arranged within a crystal.
- Sulphur makes up almost 3% of the Earth's mass. If you think that's not much, next time you look to the sky and see the Moon, think of this the Earth contains enough sulphur to make not just one new Moon but two.

To be continued in the next issue

NEET 2016

(PHASE II)

PRACTICE PAPER

A COLLECTION OF ASSORTED SOLVED KNOCK OUTS

INSTRUCTIONS

- This test consists of 45 questions and each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 mark will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instruction.

1. Which of the following statements is incorrect?

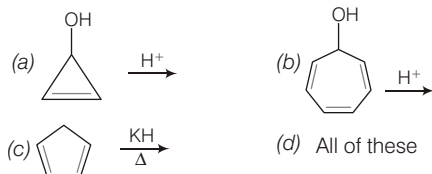
- (a) O_2 is paramagnetic with bond order 2
 (b) O_2^{2-} is paramagnetic with bond order 2
 (c) O_2^+ is paramagnetic with bond order 2.5
 (d) O_2^- has one unpaired electron with bond order 1.5

2. Which of the following statements is/are incorrect in the case of heavy water?

- I. Heavy water has lower boiling point than ordinary water.
 II. Heavy water is used as a moderator in nuclear reactor.
 III. Heavy water is more effective as solvent than ordinary water.
 IV. Heavy water is more associated than ordinary water.

- (a) I and IV
 (b) I and III
 (c) Only I
 (d) Only IV

3. Which of the following reaction products formed is aromatic?



4. The complex of $[Co(NH_3)_5(NO_2)]^{2+}$ shows

- (a) optical isomerism (b) geometrical isomerism
 (c) ionisation isomerism (d) linkage isomerism

5. A new carbon-carbon bond formation is possible in

- (a) Cannizzaro reaction (b) Decarboxylation reaction
 (c) Clemmensen reduction (d) Reimer-Tiemann reaction

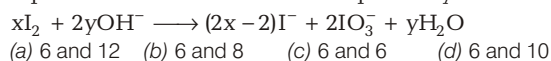
6. Electromagnetic radiations of wavelength 328 nm are just sufficient to ionise sodium atom. The ionisation energy of sodium in kJ mol^{-1} is

- (a) 461.4 (b) 361.4 (c) 261.4 (d) 561.4

7. Which of the following statement is correct?

- (a) CO_2 and SiO_2 both are gases
 (b) CO_2 is gas and SiO_2 is a liquid
 (c) CO_2 is a gas but SiO_2 is a solid
 (d) Carbon and Si both form oxides of similar properties

8. The value of x and y for the following balanced equation in alkaline medium respectively are



9. The equilibrium constant for the reaction $Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$ is

(Given, $E^\circ_{(Ce^{4+}/Ce^{3+})} = 1.44 \text{ V}$, $E^\circ_{(Fe^{3+}/Fe^{2+})} = 0.68 \text{ V}$)

- (a) 4.26×10^{35} (b) 3.44×10^{12}
 (c) 4.26×10^{24} (d) 6.88×10^{12}

10. A plot of logarithm of rate versus logarithm of concentration of the reactant in a first order reaction is straight line whose slope is $\tan \theta$, where θ is
 (a) 45° (b) 135° (c) 90° (d) $\log K$

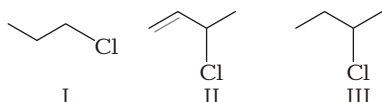
11. Select the incorrect statement.

- (a) Sucrose is dextrorotatory with specific rotation of $+166.5^\circ$
 (b) Phenomenon of change in specific rotation to a constant value is called mutarotation.
 (c) Cellulose is a white solid and main constituent of plants
 (d) Cellulose on complete hydrolysis gives D-(+)-glucose

12. By plotting compressibility factor, Z vs p at a constant temperature, behaviour of a real gas is depicted. At high temperature and pressure, $Z > 1$. This fact can be explained by van der Waals' equation when

- (a) the constant a is negligible
 (b) the constant b is negligible
 (c) Both the constants a and b are negligible
 (d) Both the constants a and b are not negligible

13. The decreasing order of the following chlorides towards S_N1 reaction is



- (a) $I > II > III$ (b) $III > II > I$
 (c) $II > III > I$ (d) $II > I > III$

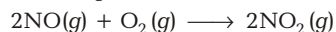
14. Which of the following statements is/are correct?

- I. Fluorine does not form oxide with oxygen but it forms oxygen fluoride.
 II. Among all the hydrogen halides, HF is more volatile while HCl is least volatile.
 III. Dissociation energy of F_2 is lesser than that of Cl_2 .
 IV. Sodium thiosulphate does not discharge the colour of iodine solution.
 (a) II and IV (b) I and II (c) I and III (d) Only II

15. Which one of the following is the correct statement?

- (a) $B_3N_3H_6$ is known as inorganic benzene
 (b) Chlorides of both beryllium and aluminium have bridged structure in gas phase
 (c) Boric acid is a protonic acid
 (d) Beryllium exhibits coordination number of six

16. The reaction between nitric oxide (NO) and oxygen to form nitrogen dioxide (NO_2) is a key step in photochemical smog formation



The grams of NO_2 are formed by complete reaction of 1.20 g NO is

- (a) 7.2 g (b) 2.3 g (c) 1.8 g (d) 4.1 g

17. The solubility of fluorides of alkali metals in water is

- (a) $LiF > NaF > KF > RbF > CsF$
 (b) $CsF > RbF > KF > NaF > LiF$
 (c) $LiF > KF > NaF > CsF > RbF$
 (d) $CsF > KF > NaF > RbF > LiF$

18. Which of the following statements is incorrect?

- (a) Aqueous solution of Na_2CO_3 is less basic than aqueous solution of $NaHCO_3$
 (b) The orange solution of $Na_2Cr_2O_7$ becomes yellow on addition of NaOH
 (c) $Al(OH)_3$ is insoluble in excess of NH_4OH but soluble in NaOH
 (d) Both (b) and (c)

19. When I^- is oxidised by MnO_4^- in alkaline medium I^- converts into

- (a) IO_3^- (b) I_2 (c) IO_4^- (d) IO^-

20. Wave number of a spectral line for a given transition is $x \text{ cm}^{-1}$ for He^+ , then its value for Be^{3+} (isoelectronic of He^+) for same transition is

- (a) $x \text{ cm}^{-1}$ (b) $4x \text{ cm}^{-1}$ (c) $\frac{x}{4} \text{ cm}^{-1}$ (d) $2x \text{ cm}^{-1}$

21. Match the following and choose the correct option.

Column I	Column II
A. Ribose	1. Ninhydrin
B. Biotin	2. Nucleic acid
C. Enzyme	3. Vitamin
D. Glycine	4. Globular protein

Codes

- | | | | | | | | |
|-------|---|---|---|-------|---|---|---|
| A | B | C | D | A | B | C | D |
| (a) 1 | 4 | 2 | 3 | (b) 2 | 3 | 4 | 1 |
| (c) 1 | 2 | 3 | 4 | (d) 2 | 3 | 1 | 4 |

22. A polymer is made of 30% molecules of molar mass 20000; 40% molecules of molar mass 30000 and rest have 60000. Calculate the number average and weight average of molecular masses.

- (a) 36000;43333 (b) 48000;5666
 (c) 43333;36000 (d) 56666;48000

23. Match the following Column I with Column II.

Column I (Colloidal of dispersion)	Column II (Nature of dispersion)
A. Milk	p. Solid in liquid
B. Clouds	q. Liquid in gas
C. Paints	r. Solid in solid
D. Jellies	s. Liquid in liquid
	t. Liquid in solid

Codes

- | | | | | | | | |
|-------|---|---|---|-------|---|---|---|
| A | B | C | D | A | B | C | D |
| (a) s | q | p | t | (b) p | t | r | q |
| (c) s | t | p | q | (d) p | q | r | t |

24. Which of the following statements is correct?

- (a) Aniline is a stronger base than ethyl amine
 (b) Aniline is a stronger base than *p*-methane aniline
 (c) Aniline must be acetylated before nitration with an acid derivative
 (d) Aniline is soluble in an ammonium hydroxide solution

 EXAM SPECTRUM

25. Among the following molecules,
I. XeO_3 II. XeOF_4 III. XeF_6
those having same number of lone pairs on Xe are

(a) I and III
(b) I and II
(c) II and III
(d) I, II and III

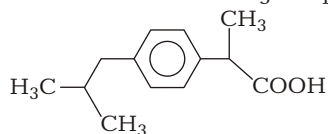
26. The number of β -particles emitted during the transformation of ${}^x_y A$ to ${}^m_n B$ is

(a) $\frac{n-m}{4}$ (b) $n + \frac{x-m}{4} + y$
(c) $x + \frac{x-m}{4} + y$ (d) $2y - n + x - m$

27. In the cyanide extraction process of silver from argentite ore, the oxidising and reducing agents used are

(a) O_2 and CO respectively
(b) O_2 and Zn dust respectively
(c) HNO_3 and Zn dust respectively
(d) HNO_3 and CO respectively

28. The IUPAC name of the following compound is

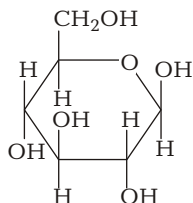


(a) 2-(4-isobutyl phenyl) propanoic acid
(b) 2-(*p*-sec-butyl phenyl) propanoic acid
(c) 3-(*p*-isobutyl phenyl) propanoic acid
(d) 3-(*p*-sec-butyl phenyl) propanoic acid

29. The correct order of ionic radii of Yb^{3+} , La^{3+} , Eu^{3+} and Lu^{3+} is

(a) $\text{Yb}^{3+} < \text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+}$
(b) $\text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+} < \text{Yb}^{3+}$
(c) $\text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+} < \text{Yb}^{3+}$
(d) $\text{Yb}^{3+} < \text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+}$

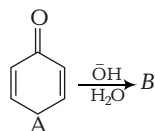
30. The following carbohydrate is very important for human body,



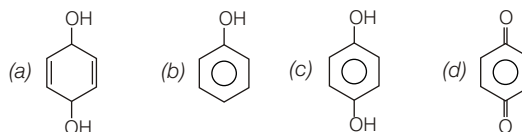
Anomeric carbon present in the carbohydrate are

(a) 1 (b) 2
(c) 3 (d) 4

31. Consider the following reaction,



Identify the product B.



32. The enolic form of acetone contains
(a) 10 σ -bonds, 2 π -bonds and 1 lone pair
(b) 9 σ -bonds, 2 π -bonds and 2 lone pairs
(c) 8 σ -bonds, 2 π -bonds and 2 lone pairs
(d) 9 σ -bonds, 1 π -bond and 2 lone pairs

33. The magnetic moment of M^{x+} (atomic number = 25) is $\sqrt{15}$ BM. Then, the oxidation number x of M is

(a) 3 (b) 4
(c) 2 (d) 1

34. In terms of Arrhenius equation, $k = Ae^{-E_a/RT}$ the temperature dependence of rate constant (k) of a chemical reaction is written. Then, the activation energy (E_a) of the reaction can be calculated by plotting.

(a) $\log k$ vs $\frac{1}{\log T}$
(b) $\log k$ vs $\frac{1}{T}$
(c) k vs T
(d) k vs $\frac{1}{\log T}$

35. The temperature of the slag zone in the metallurgy of the iron using blast furnace is

(a) 1500-1600°C (b) 400-700°C
(c) 800-1000°C (d) 1200-1000°C

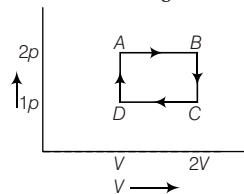
36. Pick up the incorrect statement.

(a) The boiling points of alkyl halides are more than those of the corresponding alkanes
(b) In water, the solubility order of alcohols is, $\text{CH}_3\text{OH} > \text{C}_2\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{OH}$
(c) $\text{C}_6\text{H}_5\text{NH}_2$ is a weaker base than NH_3
(d) All of the above statements are wrong

37. Polarising action of Cd^{2+} on ion is stronger than that of Ca^{2+} because

(a) the charges of the ions are same
(b) their radii are same
(c) they have complete electronic energy shells configuration
(d) All of the above options are correct

38. An ideal monoatomic gas follows the path ABCD. Then, the work done during the complete cycle is



(a) zero (b) $-\frac{1}{2} pV$
(c) $-pV$ (d) $-2 pV$

39. Which of the following relation is correct for gaseous and reversible reactions?
- (a) $\frac{K_C}{K_p} = (RT)^{\Delta n_g}$ (b) $\frac{K_p}{K_x} = (p)^{\Delta n_g}$
- (c) $\frac{K_C}{K_x} = (p)^{-\Delta n_g}$ (d) $\frac{K_C}{K_x} = \left(\frac{p}{RT}\right)^{\Delta n_g}$
40. Which one of the following statements about the zeolites is/are correct?
- (a) They are used as cation exchangers
 (b) They have open structure which enables them to take up small molecules
 (c) Zeolites are aluminosilicates having three-dimensional network
 (d) All are correct
41. Which one of the following orders represents the correct sequence of the decreasing acidic nature of the given oxide?
- (a) $\text{MgO} < \text{K}_2\text{O} < \text{Al}_2\text{O}_3 < \text{Na}_2\text{O}$
 (b) $\text{Al}_2\text{O}_3 > \text{MgO} > \text{Na}_2\text{O} > \text{K}_2\text{O}$
- (c) $\text{Na}_2\text{O} < \text{K}_2\text{O} < \text{MgO} < \text{Al}_2\text{O}_3$
 (d) $\text{K}_2\text{O} > \text{Na}_2\text{O} > \text{Al}_2\text{O}_3 > \text{MgO}$
42. The total pressure in a mixture of 9 g of dioxygen and 5 g of dihydrogen confined in a vessel of 1 dm^3 at 27°C is ($R = 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$)
- (a) 79.52 (b) 6.952 (c) 69.25 (d) 59.25
43. Commonly used catalyst in the preparation of acrylonitrile from propylene and ammonia is
- (a) silver (b) bismuth molybdate
 (c) cerium chloride (d) nickel
44. The one which has least iodine value is
- (a) ginger oil (b) ghee
 (c) groundnut oil (d) sunflower oil
45. Sodium crystallises in bcc arrangement with the interfacial separation between the atoms at the edge of 53 pm. The density of the solid is
- (a) 1.23 g/cc (b) 4.85 g/cc
 (c) 4.85 g/cc (d) 1.23 g/cc

Answers

1. (b) 2. (a) 3. (d) 4. (d) 5. (d) 6. (b) 7. (c) 8. (c) 9. (d) 10. (a)
11. (a) 12. (a) 13. (c) 14. (c) 15. (a) 16. (c) 17. (b) 18. (a) 19. (a) 20. (b)
21. (b) 22. (a) 23. (a) 24. (c) 25. (d) 26. (c) 27. (b) 28. (a) 29. (d) 30. (a)
31. (b) 32. (d) 33. (b) 34. (b) 35. (c) 36. (d) 37. (c) 38. (c) 39. (b) 40. (d)
41. (b) 42. (c) 43. (b) 44. (b) 45. (a)

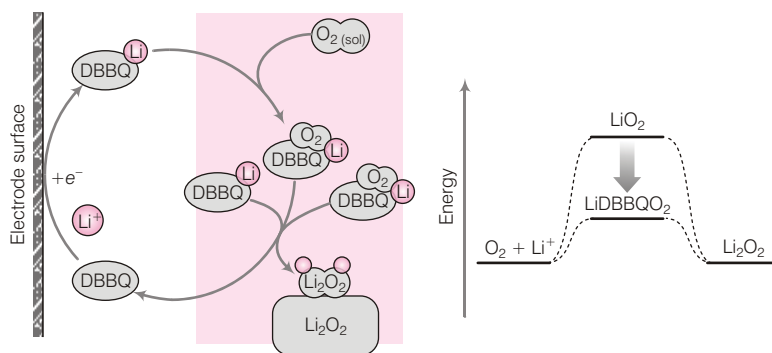
CHEMISTRY IN action

Lithium-air batteries : A new hope

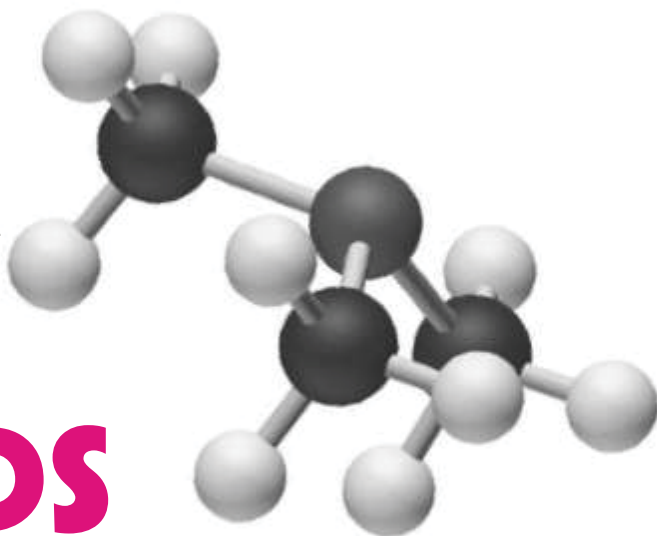
Lithium-ion batteries are a mainstay in electronic devices because they have a long lifespan and can discharge at high voltages. But lithium-ion batteries still have some limitations, leading scientists to explore other possibilities involving lithium. One enticing possibility is the lithium-air battery. The practical lithium-air battery's energy storage is predicted to be three-to-four-fold higher than that of today's lithium-ion batteries. This high energy storage makes it an excellent candidate for powering electric cars.

However, lithium-air batteries have several hurdles to overcome before they can become practically useful. In order to make a stable Li-O₂ battery, the electrolyte solution needs to be a low-polarity (weakly solvating) solvent. Unfortunately, using such solvents also limits the battery performance by unacceptable levels due to product formation on the cathode surface.

Researchers have added DBBQ (2,5-di-tert-butyl-1,4-benzoquinone) to a weakly solvating electrolyte solution, LiTFSI in ether, and found that not only did this electrolyte solution prevent deposits on the cathode surface, leading to a much higher energy storage (80-to-100-fold increase), but it also increased the reaction rate. Schematics of reactions on discharge (left) and the effect of DBBQ on the potential determining step (right)



NOMENCLATURE OF ORGANIC COMPOUNDS



THIS SECTION IS TARGETTED TO PROVIDE AN INSIGHT OF IUPAC NOMENCLATURE OF ORGANIC AND INORGANIC COMPOUNDS THROUGH QUESTIONS AS EVERY YEAR ATLEAST 1-2 QUESTIONS ARE ASKED ON IUPAC NOMENCLATURE IN ALL COMPETITIVE EXAMS AND BOARDS.

To standardise the naming of organic compounds, IUPAC has proposed some rules that are accepted all over the world. The IUPAC name of any organic compound can be written by the use of following formula:

2°-prefix + 1°-prefix + word root + 1°-suffix + 2°-suffix.

Here, **word root** represents the number of carbon atoms present in the principal chain.

1°-suffix represents saturation or unsaturation in longest possible carbon chain.

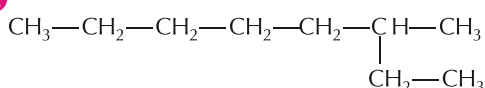
2°-suffix represents nature of functional group.

1°-prefix represents acyclic or cyclic nature of the compound.

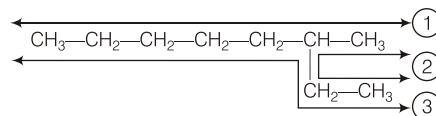
2°-prefix represents substituents that are not treated as functional group.

First let us learn how the longest possible chain of C-atoms is selected in organic compounds. Let us take some examples:

Example 1

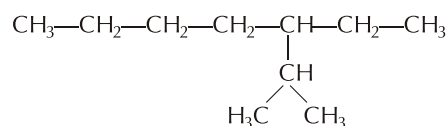


Sol. Rule The chain with maximum number of carbon atoms will be the longest possible chain.

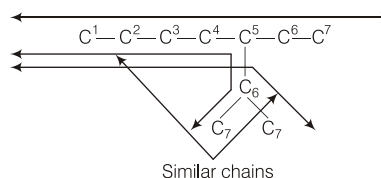


- Chain 1 has 7 carbon atoms.
- Chain 2 has 4 carbon atoms.
- Chain 3 has 8 carbon atoms.
- Here, principal chain will be chain 3.

Example 2

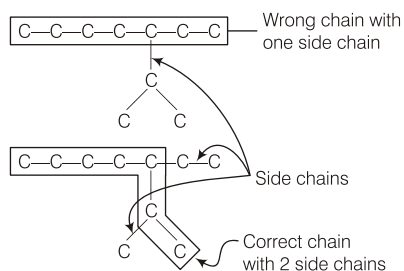


Sol. Rule In case of two or more chains with same number of C-atoms, select the chain with maximum number of side chains as the longest possible chain (IUPAC prefers such a situation to avoid complicated names).

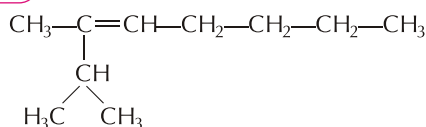


In this example, all the possible 3 chains contain 7 C-atoms in them. Out of these 3, two chains are similar as seen in diagram.

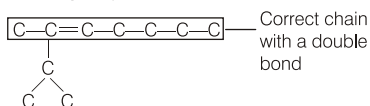
So, here



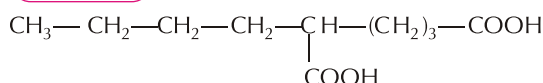
Example 3



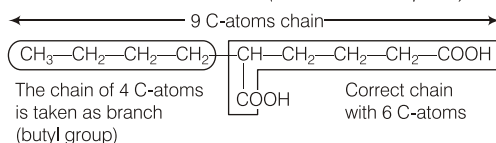
Sol. Rule If a double bond/triple bond/functional group is present in the molecule, then it must be included in the longest possible chain.



Example 4



Sol. Rule Avoid the longest chain rule if the chain containing multiple bonds or functional group falls smaller than other chains (the rule of exception).



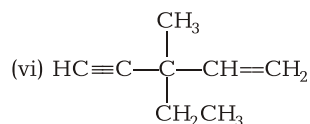
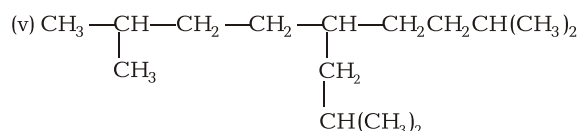
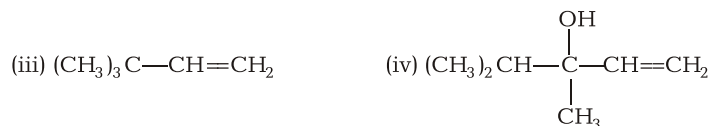
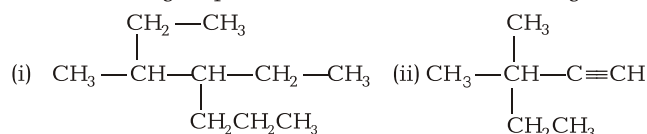
In this particular case, although the longest chain is of 9 C-atoms but the preference will be given to the chain of 6C-atoms.

Functional Groupwise Nomenclature

Organic compound	IUPAC name
Alkane	Root word + -ane = alkane
Alkene	Alkane - ane + ene = alkene
Alkyne	Alkane - ane + yne = alkyne
Alcohols	Alkane - e + ol = alkanol
Aldehydes	Alkane - e + al = alkanal
Ketones	Alkane - e + one = alkanone
Carboxylic acids	Alkane - e + oic acid = alkanonic acid
Acid chloride	Alkanoic acid - ic acid + yl chloride = alkanoyl chloride
Acid anhydride	Alkanoic acid - acid + anhydride = alkanonic anhydride
Amides	Alkanoic acid - oic acid + amide = alkanamide
Sulphonic acid	Alkane + sulphonic acid = alkane sulphonic acid
Nitro compounds	Nitro + alkanes = Nitroalkanes
Cyanides or nitriles	Alkane + nitrile = Alkane nitrile

Practice Problems

Select the longest possible chain from the following.



Notice Board

No weightage to class XII marks from 2017

HRD minister officials said that, class XII marks will not be a factor for determining rankings in the Joint Entrance Examination (JEE) for admissions to engineering undergraduate courses from next year.

Class XII scores will be a crucial parameter only for determining the eligibility criteria for the exam. To qualify for appearing in exam, students need to have atleast 75% marks or be in top 20 percentile in class XII examination. SC, ST students should have 65% marks.

SOLID STATE

- Possesses definite shape and volume.
- Characterised by low compressibility and vapour pressure with definite melting point.
- Shows high rigidity, mechanical strength and density with slow diffusion. The constituent particles of solid are very closely packed to attain a minimum potential energy which results intermolecular distances become very small between constituent particles.

TYPES OF SOLIDS

(I) CRYSTALLINE SOLIDS

- These are composed with particles in an orderly repetitive array.
- These are homogeneous anisotropic (different physical properties in different directions) substances with a definite geometrical shape.
- These have a definite and characteristic heat of fusion.

(II) AMORPHOUS SOLIDS

- The constituent particles are not arranged in a regular manner.
- These are isotropic (same physical properties in all directions) substances without definite geometrical shape.
- These do not have a definite heat of fusion.

CLASSIFICATION OF CRYSTALLINE SOLIDS

- Ionic crystals** These have positive and negative ions as constituent particles which are bonded to each other by strong electrostatic forces of attraction, e.g. $\text{Na}^+ \text{Cl}^-$.
- Molecular crystals** These have molecules as constituent particles which are bonded by van der Waals' forces, e.g. I_2 .
These are further subdivided into the following three categories:
 - (a) Non-polar molecular solids, e.g. H_2, Cl_2 .
 - (b) Polar molecular solids, e.g. solid SO_2 , solid NH_3 .
 - (c) Hydrogen bonded molecular solids, e.g. $\text{H}_2\text{O}, \text{HF}$.
- Covalent crystals** These have atoms as constituent particles which are bonded together by covalent bonds, e.g. diamond, graphite.
- Metallic crystals** These have positive metal ions (kernels) and free electrons as constituent particles which are bonded together by metallic bonds. e.g. all metals and alloys.

LAWS OF CRYSTALLOGRAPHY

The study of structure, geometry and properties of crystalline structures is called crystallography and is governed by the following laws:

Steno's law The interfacial angle of a crystal for a particular substance always remains same.

The law of symmetry All crystals of same substance possess the same element of symmetry. A crystalline substance has the following three elements of symmetry:

- (i) Centre of symmetry
- (ii) Plane of symmetry
- (iii) Axis of symmetry

Note The sum of the numbers of plane, axis and centre of symmetries possessed by a crystal is called elements of symmetry of that crystal. e.g. for cubic crystals, there are 9 plane of symmetry, 13 axis of symmetry and 1 centre of symmetry, making the elements of symmetry equals to $9 + 13 + 1 = 23$.

BRAGG'S LAW

When a beam of monochromatic X-ray strikes two planes of atoms in a crystal at a certain angle θ and reflected, the intensity of reflected beam is maximum when

$$n\lambda = 2d \sin \theta \text{ (for constructive interference)}$$

$$n\lambda = 4d \sin \theta \text{ (for destructive interference)}$$

where, n = order of diffraction ($n \in I^+$), d = distance between two planes, λ = wavelength of X-ray, θ = angle between X-ray and plane of crystal (angle of diffraction).

Effective number of atoms in a unit cell

$$\text{Number of atoms per unit cell } (Z) = \frac{n_c}{8} + \frac{n_f}{2} + \frac{n_i}{1}$$

where, n_c = number of atoms at the corners of the cube
 n_f = number of atoms at six faces of the cube
 n_i = number of atoms inside the cube

Note For a hexagonal unit cell, atoms present at corners, edges, faces and centre are shared by 6, 3, 2 and 1 unit cells, respectively. Hence, for hexagonal lattice,

$$Z = \frac{n_c}{6} + \frac{n_e}{3} + \frac{n_f}{2} + \frac{n_i}{1}$$

PACKING IN SOLIDS

- Packing in solids is expressed in terms of packing fraction.

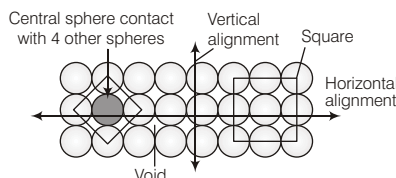
Packing fraction (PF)

$$= \frac{\text{Total volume of spheres}}{\text{Volume of the unit cell}} \times 100$$

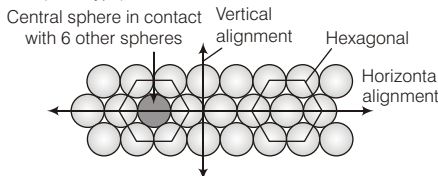
- The number of spheres surrounding a particular atom is known as its coordination number (CN).

TYPES OF PACKING IN SOLIDS

- Packing in 1D** Atoms are arranged in a row touching each other.
- Packing in 2D** Atoms are arranged in more than one row by stacking one dimensional closed packed structure.



Square close packing of spheres in two dimensions (AAA...type)

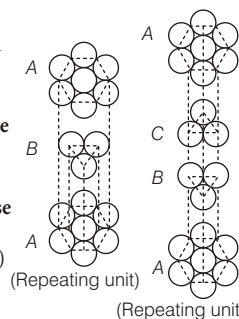


Hexagonal close packing of spheres in two dimensions (ABAB...type)

- Packing in 3D** The structure obtained by stacking 2D layers one above the other.

There are following two types of 3D closed packing:

- 3D closed packing from 2D square closed packed layers** This is also known as AAA type arrangement. The generated cubic lattice is called simple cubic lattice and unit cell is known as simple or primitive unit cell.
- 3D close packing from 2D hexagonal close packed structure**
 - Hexagonal close packing (ABAB... pattern)**
 - Cubic close packing (ABCABC... pattern)**



CONCEPTS your Revision SOLID

Unit cell It is the smallest repeating unit of a crystal which Details about different unit cell parameters are given below.

Unit cell type	Position of constituent particles	Radius of atom (r)	Volume of unit cell (V)	Vol at ur
Simple cubic	At corners	$\frac{a}{2}$	a^3	
bcc	At corners and body centre	$\frac{\sqrt{3}a}{4}$	a^3	
fcc	At corners and face-centres	$\frac{a}{2\sqrt{2}}$	a^3	
Hexagonal unit cell (hcp)	At corners, edges, faces and centre	$r = \frac{a}{2}$ $r = \sqrt{3/2} \times h/4$	$3\sqrt{2}a^3$	

where, a = edge length of unit cell, h = height of hexagonal

DENSITY OF A CRYSTAL (d)

$$d = \frac{nM}{N_A} \times \frac{1}{V} = \frac{nM}{N_A a^3} \text{ g cm}^{-3}$$

where, n = number of atoms in a unit cell
 a = edge length of unit cell
 M = molecular mass of crystal
 N_A = Avogadro's number

VOIDS IN SOLIDS

In closely packed structures, the empty space is called interstitial site or void. These are of the following types:

Trigonal void Empty space among three spheres touching each other in 2D space.

Tetrahedral void (TV) It is produced when one sphere is placed over three other spheres touching each other.

Octahedral void (OV) It is produced when three spheres are exactly placed over another three spheres.

Note • Number of tetrahedral voids = $2 \times$ Number of atoms in ccp = $2N$

• Number of octahedral voids = Number of atoms in ccp = N

• Regular TVs and OVs are found in hcp and ccp, whereas distorted TVs and OVs are found in bcc structures.

• Coordination numbers of an atom in TVs and OVs are 4 and 6, respectively.

VOIDS in Different Unit Cells

Types of unit cell	sc	fcc	bcc
Arrangement of atoms/ions	At each corner	At each corner + face centre	At corner + body centre

POINT MAP Classification Tool STATE

is repeated over and over again in different directions.

Volume of all atoms in a unit cell (V)	Packing fraction (v/V)	Coordination number (CN)	d in terms of r
$\pi \frac{a^3}{6}$	52% $\left(\frac{\pi}{6}\right)$	6	$\frac{M_0}{8N_A r^3}$
$\frac{\sqrt{3}\pi a^3}{8}$	68% $\left(\frac{\sqrt{3}\pi}{8}\right)$	8	$\frac{2M_0}{N_A \times (4r/\sqrt{3})^3}$
$\frac{\pi a^3}{3\sqrt{2}}$	74% $\left(\frac{\pi}{3\sqrt{2}}\right)$	12	$\frac{4M_0}{N_A \times (2\sqrt{2}r)^3}$
πa^3	74% $\left(\frac{\pi}{3\sqrt{2}}\right)$	12	$\frac{6M_0}{3\sqrt{2}(2r)^3 N_A}$

Types of unit cell	sc	fcc	bcc
Atoms/ions per unit cell (Z_{eff})	$8 \times \frac{1}{8} = 1$	$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$	$8 \times \frac{1}{8} + 1 = 2$
Types of voids	Cubic void	4 TVs and 8 OVs per unit cell	Distorted TVs and OVs
Radius ratio (r_v/r)	$(\sqrt{3}-1) = 0.732$	0.225 for TV, 0.414 for OV	0.29 for TV, 0.1547 for OV

where, r_v = radius of void, r = radius of atom

Relations between Radius Ratio and Coordination Number

Radius ratio	Types of void	Coordination number(CN)	Example
0.155-0.225	Trigonal void	3	B_2O_3
0.225-0.414	TV	4	ZnS
0.414-0.732	OV	6	NaCl
0.732-1.0	Cubic void	8	CsCl

Note A simple cubic unit cell has a single cubic void in the centre

$$\text{Radius ratio} = \frac{\text{Radius of cation}}{\text{Radius of anion}}$$

DEFECTS IN SOLIDS

Any deviation from perfectly ordered arrangement of constituents of a solid is known as imperfections or defects in solids.

These are of two types :

- Point defects** Deviation from ideal arrangement around a point or an atom.
- Line defects** Deviation from ideal arrangement in entire rows of lattice points.

TYPES OF POINT DEFECTS

- Stoichiometric/Intrinsic thermodynamic** Does not disturb stoichiometry of solid.
- Impurity** Arise when foreign atoms are present at lattice sites.
- Non-stoichiometric** Disturb stoichiometry of solids.

TYPES OF STOICHIOMETRIC DEFECTS

Vacancy Arise when lattice sites are vacant, decreases density, shown by non-ionic solids.

Interstitial Arise when constituent particles occupy interstitial site, increases density, shown by non-ionic solids.

Frenkel Smaller ion (usually cation) dislocates from its interstitial site, does not change density, shown by ionic solids, e.g. ZnS.

Schottky Arise when lattice sites are vacant, decreases density, shown by ionic solids, e.g. CsCl.

TYPES OF NON-STOICHIOMETRIC DEFECTS

METAL EXCESS

Due to anionic deficiency Arise due to loss of electron by metal ion to form cation. This electronic is trapped in the anionic vacancy known as F-centre, e.g. LiCl.

Due to presence of extra cations Usually arise when metal oxides are heated, e.g. ZnO.

METAL DEFICIENCY

Arise when metal shows variable valencies, e.g. Fe^{2+} , Fe^{3+} .

ELECTRICAL PROPERTIES OF SOLIDS

Solids are classified into three groups on the basis of conduction power of electrons.

- Conductors** Conductivity is in the order of $10^7 \Omega^{-1} m^{-1}$. The conduction band is almost overlapped with valence band.
- Semiconductors** Conductivity is in the order of $10^{-6} - 10^4 \Omega^{-1} m^{-1}$. The gap between valence band and conduction band is small.

• **n-type semiconductor** This type of semiconductor is formed when group 14 elements are doped with group 15 elements. Their conductivity is due to the

extra excess electron of group 15 elements after formation of four covalent bonds.

• **p-type semiconductor** This type of semiconductor is formed when group 13 elements are doped with group 14 elements. Their conductivity is due to the positive hole generated because of group 13 elements after formation of three covalent bonds.

(iii) **Insulators** Conductivity is in the order of $10^{-10} - 10^{-20} \Omega^{-1} m^{-1}$, The gap between valence band and conduction band is large.

Note Superconductors are the conductors which allow electricity to pass through them without any resistance. The temperature at which a substance starts behaving as superconductors is called transition fraction temperature.

DIELECTRIC PROPERTIES OF SOLIDS

These properties are shown by insulators when placed in electric field due to generation of dipoles in them.

- Piezoelectricity** When a crystal is subjected to mechanical stress, the small magnitude of current is produced, e.g. Rochelle's salt.
- Pyroelectricity** Produced either by heating or cooling some polar crystal, e.g. cane sugar.
- Ferroelectricity** Piezoelectric crystals with permanent dipoles are said to have ferroelectricity, e.g. $BaTiO_3$.
- Anti-ferroelectricity** Piezoelectric crystals with zero dipole moment possess antiferroelectricity.
- Anti-piezoelectricity** The solids in which mechanical effect is developed by electric field.

MAGNETIC PROPERTIES OF SOLIDS

- Diamagnetic** Weakly repelled by the applied magnetic fields. All electrons are paired ($\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$), e.g. TiO_2 , NaCl.
- Paramagnetic** Attracted towards applied magnetic fields due to the presence of unpaired electrons ($\uparrow\uparrow\uparrow$), e.g. O_2 , Cu^{2+} .
- Ferromagnetic** Acts as permanent magnet even after removing magnetic field due to all unpaired electrons ($\uparrow\uparrow\uparrow$), e.g. Fe, Ni.
- Anti-ferromagnetic** Net dipole moment becomes zero due to equal and opposite alignment of electrons ($\uparrow\downarrow\uparrow\downarrow$), e.g. CoO , Co_3O_4 .
- Ferrimagnetic** Arises when there is net dipole moment ($\uparrow\downarrow\downarrow\uparrow\downarrow$), e.g. Fe_3O_4 , ferrites.

Various parameters for different type of structures

Types of structure	NaCl type	CsCl type	ZnS type	Fluorite (CaF_2) type	Antifluorite (Na_2O) type
Position of cations per unit cell	All OVs ($4 Na^+$)	Body centred of bcc ($1 Cs^+$)	Alternate TVs ($4 Zn^{2+}$)	fcc ($4 Ca^{2+}$)	All TVs (8)
Position of anions per unit cell	fcc ($4 Cl^-$)	Each corner of bcc ($1 Cl^-$)	fcc ($4 S^{2-}$)	All TVs ($8 F^-$)	fcc ($4 O^{2-}$)
Compounds per unit cell (Z_{eff})	4	1	4	4	4
Radius ratio (r^+/r^-)	0.414	0.732	0.225	0.225	0.225
CN and packing fraction	6 for both Na^+ and Cl^- , 0.79	8 for both Cs^+ and Cl^- , 0.72	4 for both Zn^{2+} and S^{2-} , 0.75	8 for Ca^{2+} and 4 for F^- , 0.75	4 for Na^+ and 8 for O^{2-} , 0.75
Examples	Halides of Li, Na, K etc.	Halides of Cs, TiCl, TiBr etc.	BeS, BeO, CaO etc.	$BaCl_2$, BaF_2 , $CaCl_2$, SrF_2 etc.	Li_2O , Na_2O , K_2O , Rb_2O etc.



LAWS RELATED TO SOLUTION

THIS ARTICLE IS VERY IMPORTANT FROM BOTH ENGINEERING AND MEDICAL ENTRANCE EXAMS POINTS OF VIEW. THERE ARE SOME BASIC LAWS RELATED TO VAPOUR PRESSURE OF SOLUTIONS WHICH WE SHALL DISCUSS IN THIS ARTICLE. THESE LAWS GIVE US SOME IMPORTANT INFORMATIONS ABOUT SOLUTION. SO, BEFORE READING THESE LAWS, WE MUST KNOW, WHAT IS THE VAPOUR PRESSURE OF SOLUTION?

Vapour Pressure of Solutions

It is defined as the pressure exerted by the vapours of a solvent while in equilibrium with pure solvent, at a given temperature.

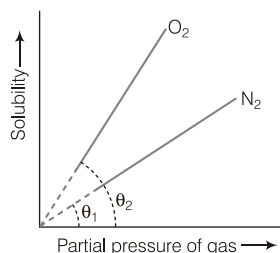
Some Facts about Vapour Pressure

- Pure liquid always has a vapour pressure higher than the solution.
- Liquids which have weak intermolecular forces are volatile and have greater vapour pressure.
- The vapour pressure of liquid increases with increase in temperature.
- When a liquid contains a solute, some of the solvent molecules are replaced by the solute particles on the surface area of liquid, therefore, the available surface area for the escape of solvent molecules decreases.
Due to less available surface area on the surface of liquid for escape, rate of evaporation as well as rate of condensation both lower down.

Laws Related to Vapour Pressure of Solutions

(A) Henry's Law

According to this law, "solubility of any gas in a liquid increases as the partial pressure (pressure exerted by a particular component to the mixture) of the gas increases.



If m g gas is dissolved in a definite amount of liquid at temperature T , the partial pressure of gas over the solvent is p atm, then

$$m \propto p \quad \text{or} \quad m = K_H p$$

When $p = 1$ atm, $m = K_H$

Here, K_H = proportionality constant which is termed as Henry's constant

p = partial pressure of gas

Unit of K_H = $\text{mol L}^{-1} \text{atm}^{-1}$ (When amount of gas and solvent are taken in moles and litres respectively)

K_H = $\text{gL}^{-1} \text{atm}^{-1}$ (When amount of gas and solvent are taken in gram and litre respectively)

- If solubility(s) or mass(m) of a gas is known at one particular pressure, then it can be calculated at other pressure using the following relation,

$$\frac{m_1 \text{ or } s_1}{m_2 \text{ or } s_2} = \frac{p_1}{p_2}$$

Note Mole fraction (χ) of the gas in a solution is directly proportional to the partial pressure (p) of the gas. Different gases have different values of K_H at a definite temperature,

$$\text{i.e.} \quad \chi \propto p$$

$$\text{or} \quad \chi = Kp$$

$$\text{or} \quad p = \frac{1}{K} \chi \quad \left[\text{Here, } \frac{1}{K} = K_H = \text{Henry's constant} \right]$$

$$\text{or} \quad p = K_H \chi$$

Conditions of Gases to Obey Henry's Law

- There should not be any chemical reaction between gas and solvent.
- The temperature should not be too low.
- The pressures or concentrations should not be too high.
- The gas must remain in its molecular state, i.e. neither gets dissociate nor associate.

IMPORTANCE OF HENRY'S LAW

- In avoiding toxic effects of high concentration of nitrogen in blood** Nitrogen gas is a more soluble gas in our blood and at deep sea, pressure increases, so solubility of N_2 gas also increases. When scuba diver tries to come rapidly towards the surface of water, pressure decreases and dissolved N_2 gas comes back from the blood and makes bubbles in his veins and causes bends. To avoid these bends, diver uses a tank that is filled with gases diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).
- In packing of soda cans** The bottles of soda water are always packed under higher pressure to increase the solubility of CO_2 gas in soda water.
- In avoiding anoxia** At higher altitudes, the partial pressure of oxygen becomes less than at the ground level because atmospheric pressure is less. Due to it, the solubility of oxygen in our blood becomes low which results anoxia (Anoxia is a medical condition in which there is a deficiency of oxygen reaching the tissues).
- In removing dissolved gases from boiler feedwater** A deaerator is a device that is used in industries for the removal of air and other dissolved gases from the feedwater to steam generating boilers. The removal of these gases is an essential process as presence of these gases in feedwater causes rapid localised corrosion in boiler tubes.

Problems Based on Henry's Law

Example 1

The solubility of N_2 in water was found to be $6.8 \times 10^{-4} \text{ mol L}^{-1}$ at 298 K temperature and 1 atm pressure. If partial pressure of N_2 is 0.78 atm, find the concentration of N_2 dissolved in water.

- (a) $5.3 \times 10^{-4} \text{ M}$ (b) $5.3 \times 10^{-5} \text{ M}$
 (c) $5.3 \times 10^{-3} \text{ M}$ (d) $5.0 \times 10^{-2} \text{ M}$

Sol. (a) From Henry's law, $s = K_H p$

$$s = 6.8 \times 10^{-4} \text{ mol L}^{-1}, p = 1 \text{ atm}$$

$$\therefore K_H = \frac{s}{p} = \frac{6.8 \times 10^{-4} \text{ mol L}^{-1}}{1 \text{ atm}} = 6.8 \times 10^{-4} \text{ mol L}^{-1} \text{ atm}^{-1}$$

At 0.78 atm, concentration of N_2 dissolved in water

$$x = K_H p'$$

$$x = 6.8 \times 10^{-4} \text{ mol L}^{-1} \text{ atm}^{-1} \times 0.78 \text{ atm}$$

$$\text{or} \quad x = 5.3 \times 10^{-4} \text{ M}$$

Example 2

The partial pressure of ethane over a saturated solution containing $6.52 \times 10^{-2} \text{ g}$ of ethane was 1 bar. If the solution contained $5 \times 10^{-2} \text{ g}$ of ethane, what should be the partial pressure of the gas?

- (a) 0.532 bar (b) 1.23 bar
 (c) 0.762 bar (d) 1.79 bar

CHEMISTRY CONCENTRATE

Sol. (c) According to Henry's law,

$$\frac{m_1}{m_2} = \frac{p_1}{p_2} \quad \dots(i)$$

Here, m_1 and m_2 are masses of ethane at p_1 and p_2 partial pressures, respectively.

From Eq. (i),

$$\frac{6.52 \times 10^{-2} \text{ g}}{5 \times 10^{-2} \text{ g}} = \frac{1}{p_2} \Rightarrow p_2 = 0.762 \text{ bar}$$

Example 3

The Henry's law constant for the stability of N_2 gas in water at 298 K is 1.0×10^5 atm. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from air dissolved in 10 moles of water at 298 K and 5 atm pressure is

[IIT JEE 2009]

- (a) 4.0×10^{-4} (b) 4.0×10^{-5}
 (c) 5.0×10^{-4} (d) 4.0×10^{-6}

Sol. (a)

$$p_{\text{N}_2} = K_H \times \chi_{\text{N}_2}$$

$$\chi_{\text{N}_2} = \frac{0.8 \times 5}{1.0 \times 10^5} \\ = 4.0 \times 10^{-5}$$

$$\therefore \frac{n_{\text{N}_2}}{n_{\text{N}_2} + n_{\text{H}_2\text{O}}} = \chi_{\text{N}_2}$$

$$\therefore \frac{n_{\text{N}_2}}{n_{\text{N}_2} + 10} = 4.0 \times 10^{-5}$$

$$n_{\text{N}_2} = (4 \times 10^{-5} \times n_{\text{N}_2}) + (4 \times 10^{-5} \times 10)$$

$$\text{or } n_{\text{N}_2}(1 - 4 \times 10^{-5}) = 4 \times 10^{-4}$$

$$\text{or } n_{\text{N}_2} \approx 4.0 \times 10^{-4}$$

[as $1 \gg 4 \times 10^{-4}$, neglect lower term]

(B) Raoult's Law

Henry's law does not hold good at high pressures and low temperatures. Hence, Raoult gives his law according to which, "the partial vapour pressure of any volatile constituent of a solution is directly proportional to its mole fraction in solution.

Let a solution contains mixture of volatile constituents A, B, C, \dots whose corresponding partial pressures are p_A, p_B, p_C, \dots in the solution.

Hence, according to Raoult's law,

$$p_A \propto \chi_A, p_B \propto \chi_B, p_C \propto \chi_C$$

$$\text{or } p_A = p_A^\circ \chi_A, p_B = p_B^\circ \chi_B$$

$$p_C = p_C^\circ \chi_C$$

Here, $p_A^\circ, p_B^\circ, \dots$ are vapour pressures of pure liquids of A, B, \dots respectively.

According to Dalton's law of partial pressures, the total pressure (p_{total}) over the solution phase in the container will be equal to the sum of the partial pressures of the components of the solution and is given as

$$p_{\text{total}} = p_A + p_B + p_C + \dots$$

Substituting values of p_A, p_B, p_C, \dots , we get

$$p_{\text{total}} = \chi_A p_A^\circ + \chi_B p_B^\circ + \chi_C p_C^\circ + \dots$$

If number of moles of constituents A, B, C, \dots are n_A, n_B, n_C, \dots respectively, then

$$\chi_A = \frac{n_A}{\Sigma n}, \chi_B = \frac{n_B}{\Sigma n}, \chi_C = \frac{n_C}{\Sigma n}, \dots$$

$$p_{\text{total}} = p_A^\circ \frac{n_A}{\Sigma n} + p_B^\circ \frac{n_B}{\Sigma n} + p_C^\circ \frac{n_C}{\Sigma n} + \dots$$

or

$$p_{\text{total}} = p_A^\circ \frac{\frac{w_A}{m_A}}{\frac{w_A}{m_A} + \frac{w_B}{m_B} + \frac{w_C}{m_C} + \dots} + p_B^\circ \frac{\frac{w_B}{m_B}}{\frac{w_A}{m_A} + \frac{w_B}{m_B} + \frac{w_C}{m_C} + \dots} + p_C^\circ \frac{\frac{w_C}{m_C}}{\frac{w_A}{m_A} + \frac{w_B}{m_B} + \frac{w_C}{m_C} + \dots}$$

Here, w_A, w_B, w_C, \dots are masses of A, B, C, \dots while m_A, m_B, m_C, \dots are their corresponding molecular masses, respectively.

Relative Lowering in Vapour Pressure of Solution Containing Non-volatile Solute Dissolved in Volatile Solvent

Let a binary solution contains a non-volatile solute A dissolved in solvent B which is volatile.

\therefore Total pressure of solution is given as

$$p_{\text{total}} = p_A^\circ \chi_A + p_B^\circ \chi_B \quad \dots(i)$$

$$p_A^\circ = 0, \text{ as } A \text{ is a non-volatile solute.}$$

$$\therefore p_{\text{total}} = p_B^\circ \chi_B = p_B^\circ (1 - \chi_A) \quad [\because \chi_A + \chi_B = 1]$$

$$\text{or } p_{\text{total}} = p_B^\circ - p_B^\circ \chi_A$$

$$\text{or } \frac{p_B^\circ - p_{\text{total}}}{p_B^\circ} = \chi_A$$

We can generalise above relation by replacing p_B° via p° .

$$\therefore \frac{p^\circ - p_{\text{total}}}{p^\circ} = \frac{n}{n + N}$$

$$n = \text{moles of solute}$$

$$N = \text{moles of solvent}$$

or relative lowering in vapour pressure

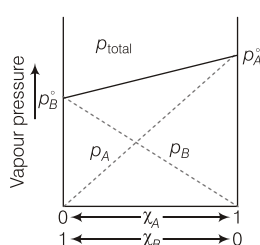
$$= \text{mole fraction of solute}$$

Limitations of Raoult's Law

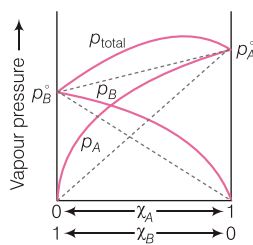
- It is valid only for very dilute solutions.
- It is valid only for the solution having non-volatile and non-electrolyte solute which exists as a single molecule.
- It is not valid for those solutes which associate or dissociate in the particular solution.

Comparison of Raoult's law between ideal and non-ideal solutions

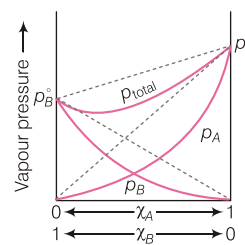
Ideal solutions	Non-ideal solutions	
	Positive deviation from Raoult's law	Negative deviation from Raoult's law
Obey Raoult's law for any concentration.	Do not obey Raoult's law	Do not obey Raoult's law
Neither heat is evolved nor heat is absorbed ($\Delta H_{\text{mix}} = 0$)	Heat is required ($\Delta H_{\text{mix}} > 0$)	Heat is evolved ($\Delta H_{\text{mix}} < 0$)
There is no change in volume ($\Delta V_{\text{mix}} = 0$).	Volume is increased after dissolution ($\Delta V_{\text{mix}} > 0$).	Volume is decreased after dissolution ($\Delta V_{\text{mix}} < 0$).
The two mixing parts are identical in shape, size and intermolecular force (i.e. $A-A$, $A-B$, $B-B$ interaction should be same).	The two mixing parts have different shape, size and intermolecular force and $A-B$ attractive force is weaker than $A-A$ and $B-B$ attractive forces.	The two mixing parts have different shape, size and intermolecular force and $A-B$ attractive force is stronger than $A-A$ and $B-B$ attractive forces.
Escaping tendency is same before and after mixing.	Escaping tendency increases after mixing, increasing vapour pressure.	Escaping tendency decreases after mixing, decreasing vapour pressure.
$p_A = p_A^\circ \chi_A$ $p_B = p_B^\circ \chi_B$ $p_T = p_A + p_B$ e.g. chlorobenzene + bromobenzene, benzene + toluene n -hexane + n -heptane, etc.	$p_A > p_A^\circ \chi_A$ $p_B > p_B^\circ \chi_B$ $p_T > p_A + p_B$ e.g. Acetone + ethanol, water + ethanol, acetone + CS_2 , acetone + benzene, etc.	$p_A < p_A^\circ \chi_A$ $p_B < p_B^\circ \chi_B$ $p_T < p_A + p_B$ e.g. Acetone + aniline, acetone + CHCl_3 , CH_3OH + CH_3COOH , water + HCl , CH_3COOH + pyridine, etc.



Plot of solution showing Raoult's law.



Plot of solution showing positive deviation from Raoult's law.



Plot of solution showing negative deviation from Raoult's law.

Strategies to Solve Problems Related to Raoult's Law

The following types of problems can be asked during exam:

Type 1 If mole fraction of a volatile component (A) is given and asked to find out partial pressure of this component, use the following formula, $p_A = p_A^\circ \chi_A$

Here, p_A , p_A° and χ_A are the partial pressure, vapour pressure in pure state and mole fraction of A , respectively.

Type 2 If vapour pressures and masses of all components are given and asked to find out total vapour pressure of solution, use the following steps:

- Find out mole fraction of each component,

$$\chi_A = \frac{n_A}{n_A + n_B + n_C + \dots}$$

$$\text{Number of moles } (n) = \frac{\text{mass (in g)}}{\text{molecular mass (g mol}^{-1}\text{)}}$$

- Find out partial pressure of each component by using formula mentioned in Type 1.
- Find out total pressure as $p_T = p_A + p_B + p_C + \dots$

Type 3 If vapour pressure of a solution is given at different conditions and asked to find out vapour pressure in pure state, make two different equations for different cases with the help of Raoult's law, solve these equations and find out vapour pressure of solution in pure state.

Type 4 When non-volatile solute is mixed with volatile solvent, relative lowering in vapour pressure of solvent occurs. If any of quantities from partial pressure of solvent (p°), total pressure of solution (p_{total}), number of moles of solute (n) or number of moles of solvent (N), mass or molecular mass of solute or solvent, is asked, use the following formula

$$\frac{p^\circ - p_{\text{total}}}{p^\circ} = \frac{n}{n + N}$$

- For dilute solutions: $n \ll N$

$$n + N \approx N \quad \text{or} \quad \frac{p^\circ - p_{\text{total}}}{p^\circ} = \frac{n}{N} = \frac{w \times M}{m \times W}$$

Here, w = Mass of solute; W = Molecular mass of solute
 m = Mass of solvent; M = Molecular mass of solvent

 CHEMISTRY CONCENTRATE

Problem Based on Raoult's Law

Example 4

The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. When a non-volatile, non-electrolyte solid weighing 2.175 g is added to 39.0 g of benzene, the vapour pressure of the solution becomes 600 mm Hg. What is the molecular weight of solid substance?

- (a) 57.03 g mol⁻¹
 (b) 65.25 g mol⁻¹
 (c) 29.73 g mol⁻¹
 (d) 60.00 g mol⁻¹

Sol. (b) According to Raoult's law,

$$p = p^\circ \chi_i$$

$$600 = 640 \left(\frac{n_1}{n_1 + n_2} \right)$$

$$\frac{n_2}{n_1} = \frac{64}{60} - 1 = \frac{1}{15}$$

or $n_2 = \frac{39}{78} \times \frac{1}{15} = 0.0333$

or $\frac{2.175}{M} = 0.0333$

$$\left(\because n_1 = \frac{\text{Weight of benzene}}{\text{Molecular weight of benzene}} \right)$$

$$\Rightarrow M = 65.25 \text{ g mol}^{-1}$$

Example 5

Two liquids A and B form ideal solution. At 300 K, the vapour pressure of a solution containing 1 mole of A and 3 moles of B is 550 mm of Hg. At the same temperature, if one more mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressure of A and B in their pure states.

- (a) 300 mm and 200 mm
 (b) 600 mm and 400 mm
 (c) 200 mm and 300 mm
 (d) 400 mm and 600 mm

Sol. (d) At 300 K,

Case I Given, Number of moles of A, $n_A = 1$

Number of moles of B, $n_B = 3$

\therefore Mole fraction of A in the ideal solution,

$$\chi_A = \frac{n_A}{n_A + n_B}$$

$$= \frac{1}{1 + 3} = 0.25$$

Similarly, mole fraction of B, $\chi_B = \frac{n_B}{n_A + n_B}$

$$= \frac{3}{1 + 3} = 0.75$$

Now according to Dalton's law of partial pressures,

$$p_{\text{total}} = p_A + p_B$$

$$= \chi_A p_A^\circ + \chi_B p_B^\circ$$

or $550 = 0.25 p_A^\circ + 0.75 p_B^\circ$... (i)

Case II When one more mole of B is added to the ideal solution at same temperature, the total vapour pressure increases by 10 mm of Hg

Hence $p'_{\text{total}} = (550 + 10) \text{ mm}$

$$= 560 \text{ mm}$$

$$n'_A = 1, n'_B = 4$$

$$\therefore \chi'_A = \frac{1}{1 + 4} = 0.20$$

$$\chi'_B = \frac{4}{1 + 4} = 0.80$$

Again from Dalton's law,

$$560 = 0.20 p_A^\circ + 0.80 p_B^\circ$$
 ... (ii)

On solving Eq. (i) and Eq. (ii), we get

$$p_A^\circ = 400 \text{ mm}$$

$$p_B^\circ = 600 \text{ mm}$$

Example 6

What weight of solute (Molecular weight = 60 g mol⁻¹) is required to dissolve it in 180 g of water to reduce the vapour pressure to $\frac{4}{5}$ th of pure water?

- (a) 120 g (b) 90 kg (c) 100 g (d) 150 g

Sol. (d) As we know, lowering in vapour pressure of a solute is given as,

$$\frac{p^\circ - p_{\text{total}}}{p_{\text{total}}} = \frac{w \times M}{m \times W}$$

$$p_{\text{total}} = \frac{4}{5} p^\circ; m = 180 \text{ g}; w = ?, W = 60 \text{ g mol}^{-1}, M = 18 \text{ g mol}^{-1}$$

$$\therefore \frac{p^\circ - \frac{4}{5} p^\circ}{\frac{4}{5} p^\circ} = \frac{w \times 18}{180 \times 60}$$

or $\frac{\frac{p^\circ}{5}}{\frac{4}{5} p^\circ} = \frac{w \times 18}{180 \times 60}$

or $w = 150 \text{ g}$



Hydrofluoric acid HF is so violently corrosive it will dissolve virtually every earthly substance including glass with the exception of polyethylene or fluorocarbon plastic, lead or platinum. But, it is still classified as a "weak acid" - a source of confusion for many. Due to its such a nature it is not kept in glass bottles.

Smart Practice

- The vapour pressure of an aqueous solution of glucose is 750 mm of Hg at 373 K. Calculate the mole fraction of solute.
(a) 0.013 (b) 0.009 (c) 0.005 (d) 0.025
- The molar volume of liquid benzene (density = 0.877 g mL⁻¹) increases by a factor of 2750 as it vaporises at 20°C and that of liquid toluene (density = 0.867 g mL⁻¹) increases by a factor of 7720 at 20°C. A solution of benzene and toluene at 20°C has a vapour pressure of 46.0 torr. Find the mole fraction of benzene in the vapours of above solution.
(a) 0.25 (b) 0.37 (c) 0.73 (d) 0.52
- An aqueous solution of glucose is prepared at 303 K by dissolving 10 g glucose in 90 g water. If vapour pressure of water is 32.8 mm Hg, what is the vapour pressure of the solution?
(a) 32.44 mm (b) 36.08 mm (c) 47.03 mm (d) 30.98 mm
- Vapour pressures of ethanol and methanol are 44.5 mm Hg and 88.7 mm Hg respectively. At the same temperature, 60 g of ethanol is mixed with 40 g of methanol forming an ideal solution. Calculate total vapour pressure of the solution.
(a) 72.32 mm (b) 66.13 mm (c) 89.02 mm (d) 90.22 mm
- K_H for H₂(g)/water system is 5.34×10^7 torr. If the partial pressure of H₂ over a solution at 25°C is 760 torr, determine the solubility of hydrogen. (Assume that density of water and solutions are same)
(a) 6.39×10^{-4} mol L⁻¹ H₂ (b) 8.79×10^{-5} mol L⁻¹ H₂
(c) 8.29×10^{-4} mol L⁻¹ H₂ (d) 7.89×10^{-4} mol L⁻¹ H₂
- Heptane and octane form an ideal solution. At 373 K, the vapour pressure of the two liquids are 105.0 kPa and 46.0 kPa, respectively. What will be the vapour pressure of the mixture of 25 g heptane and 35 g of octane?
(a) 87.23 kPa (b) 23.90 kPa (c) 72.55 kPa (d) 45.29 kPa
- Two liquids A and B show vapour pressures in the ratio of 1:2 at a certain temperature. Suppose we have an ideal solution of A and B in the mole fraction ratio A:B = 1:2, what would be the mole fraction of A in the vapour phase in equilibrium with the solution at a given temperature?
(a) 0.25 (b) 0.20 (c) 0.5 (d) 0.33
- The vapour pressure of pure liquid A at 300 K is 575 torr and that of pure liquid B is 390 torr. These two compounds form ideal liquid and gaseous mixture. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.35. Calculate the total pressure of the vapour.
(a) 575 torr (b) 440 torr (c) 490 torr (d) 390 torr
- 180 g water contains 6 g urea and 68.4 g sucrose at 298 K. If $p_{\text{H}_2\text{O}}^\circ = 23.8$ torr at 298 K, calculate vapour pressure of the solution.
($M(\text{urea}) = 60$ g mol⁻¹; $M(\text{sucrose}) = 342$ g mol⁻¹)
(a) 19.9 torr (b) 19.0 torr (c) 20.7 torr (d) 23.1 torr
- Two liquids A and B are miscible over the whole range of composition and may be treated as ideal (obeying Raoult's law). At 350 K, the vapour pressure of pure A is 24.0 kPa and pure B is 12.0 kPa. A mixture of 60% A and 40% B is distilled at this temperature. If a small amount of distillate is collected and redistilled at 350 K; what per cent of A is present in second distillate?
(a) 85.7% (b) 40.2% (c) 90.7% (d) 80.9%

Answers with Explanation

- (a) At 373 K, vapour pressure of H₂O = 760 mm Hg
According to Raoult's law,

$$\frac{p^\circ - p_s}{p_s} = \frac{n}{n + N} = \text{mole fraction of solute } (\chi_{\text{solute}})$$

$$\chi_{\text{solute}} = \frac{760 - 750}{760} = \frac{10}{760} = 0.013$$
- (c) At 20°C, volume of 1 mol (or 78 g) of benzene vapours

$$= \left(\frac{78 \times 1}{0.877} \times 2750 \right) \text{ mL}$$
 At 20°C, volume of 1 mol (or 92 g) of toluene

$$= \left(\frac{92 \times 1}{0.867} \times 7720 \right) \text{ mL}$$
 Using ideal equation,

$$pV = nRT$$

$$\frac{p_B^\circ}{760} \times \frac{78 \times 2750}{0.877 \times 1000} = 1 \times 0.0821 \times 293$$

$$p_B^\circ = 74.74 \text{ mm}$$

$$\text{Similarly, } \frac{p_T^\circ}{760} \times \frac{92 \times 7720}{0.867 \times 1000} = 1 \times 0.0821 \times 293$$

$$p_T^\circ = 22.37 \text{ mm}$$

By using Raoult's law,

$$p_m = p_B^\circ \chi_B + p_T^\circ \chi_T$$

$$p_m = p_B^\circ \chi_B + p_T^\circ (1 - \chi_B)$$

 CHEMISTRY CONCENTRATE

$$46 = 74.74\chi_B + 22.37(1 - \chi_B)$$

$$\chi_B = 0.45$$

$$\chi_B + \chi_T = 1$$

$$\chi_T = 0.55$$

Also, $p'_B = p_B^\circ \chi_B = p_m \chi'_B$

or $74.74 \times 0.45 = 46 \chi'_B$

$\therefore \chi'_B$ (in gas phase) = 0.73

3. (a) $\frac{p^0 - p_s}{p_s} = \frac{w \times M}{m \times W}$

Using the given values, $\frac{32.8 - p_s}{p_s} = \frac{10 \times 18}{180 \times 90}$

$$p_s = 32.44 \text{ mm}$$

4. (b) Both components of solution are liquid, thus

$$p_{\text{total}} = p_A^\circ \frac{\frac{w_A}{m_A} + \frac{w_B}{m_B}}{\frac{w_A}{m_A} + \frac{w_B}{m_B}} + p_B^\circ \frac{\frac{w_B}{m_B}}{\frac{w_A}{m_A} + \frac{w_B}{m_B}}$$

$$p_{\text{total}} = \left(44.5 \times \frac{\frac{60}{46} + \frac{40}{32}}{\frac{60}{46} + \frac{40}{32}} \right) + \left(88.7 \times \frac{\frac{40}{32}}{\frac{60}{46} + \frac{40}{32}} \right)$$

$$p_{\text{total}} = 66.13 \text{ mm}$$

5. (d) $\chi_{\text{H}_2} = \frac{p_{\text{H}_2}}{K_{\text{H}}} = \frac{760}{5.34 \times 10^7}$
 $= 142.3 \times 10^{-7}$

Also, $\chi_{\text{H}_2} = \frac{n_{\text{H}_2}}{n_{\text{H}_2} + n_{\text{H}_2\text{O}}} \approx \frac{n_{\text{H}_2}}{n_{\text{H}_2\text{O}}}$ [$\because n_{\text{H}_2} < n_{\text{H}_2\text{O}}$]

For 1000 g (or 1 kg) water,

$$n_{\text{H}_2\text{O}} = \frac{1000}{18} = 55.5 \text{ mol}$$

Solubility of hydrogen = $n_{\text{H}_2\text{O}} \chi_{\text{H}_2}$

$$n_{\text{H}_2} = 142.3 \times 10^{-7} \times 55.5$$

$$= 7.89 \times 10^{-4} \text{ mol L}^{-1} \text{ H}_2$$

6. (c) Molecular mass of heptane, $\text{C}_7\text{H}_{16} = 100 \text{ g mol}^{-1}$

Molecular mass of octane, $\text{C}_8\text{H}_{18} = 114 \text{ g mol}^{-1}$

Number of moles of heptane = $\frac{25}{100} = 0.25$

Number of moles of octane = $\frac{35}{114} = 0.30$

Mole fraction of heptane, $\chi_{\text{H}} = \frac{0.25}{0.25 + 0.30} = 0.45$

Mole fraction of octane, $\chi_{\text{O}} = \frac{0.30}{0.25 + 0.30} = 0.55$

The vapour pressure of mixture

$$= p_{\text{H}}^\circ \chi_{\text{H}} + p_{\text{O}}^\circ \chi_{\text{O}}$$

$$= 105.0 \times 0.45 + 46.0 \times 0.55$$

$$= 47.25 + 25.30 = 72.55 \text{ kPa}$$

7. (b) Given, $p_A^\circ : p_B^\circ = 1 : 2$

$\therefore p_A = \chi_A p_A^\circ = x \chi_A$

$p_B = \chi_B p_B^\circ = 2x \chi_B$

$p_{\text{total}} = p_A + p_B = x \chi_A + 2x \chi_B$

$\therefore \chi_A$ (vapour phase) = $\frac{p_A}{p_{\text{total}}} = \frac{x \chi_A}{5x \chi_A} = \frac{1}{5} = 0.2$

8. (b) Given, $p_A^\circ = 575 \text{ torr}$, $p_B^\circ = 390 \text{ torr}$

Let, mole fraction of A in solution = χ_A

Hence, $p_{\text{total}} = p_A^\circ \chi_A + p_B^\circ (1 - \chi_A)$... (i)

Also χ'_A = Mole fraction of A in the vapour = 0.35

$$\chi'_A = \frac{p_A^\circ \chi_A}{p_A^\circ \chi_A + p_B^\circ (1 - \chi_A)} = 0.35$$

$$= \frac{575 \chi_A}{575 \chi_A + 390 (1 - \chi_A)}$$

$$\chi_A = 0.27$$

Hence, total pressure, p_{total} from Eq. (i),

$$= 575 \times 0.27 + 390 \times 0.75 = 440 \text{ torr}$$

9. (d) By Raoult's law

$$p_{\text{solution}} = \chi_{\text{solvent}} \times p_{\text{solvent}}^\circ$$

$$p_{\text{H}_2\text{O}}^\circ = 23.8 \text{ torr}, n_{\text{H}_2\text{O}} = \frac{180}{18} = 10 \text{ mol}$$

$$n_{\text{urea}} = \frac{6}{60} = 0.1 \text{ mol}; n_{\text{sucrose}} = \frac{68.4}{342} = 0.2 \text{ mol}$$

$$\chi_{\text{solvent}} = \frac{n_{\text{water}}}{n_{\text{urea}} + n_{\text{sucrose}} + n_{\text{water}}}$$

$$= \frac{10}{0.1 + 0.2 + 10} = \frac{10}{10.3}$$

$\therefore p_{\text{solution}} = \frac{10}{10.3} \times 23.8 = 23.1 \text{ torr}$

10. (a) Given, $\chi_A = 0.60$, $p_A^\circ = 24.0 \text{ kPa}$

$$\chi_B = 0.40, p_B^\circ = 12.0 \text{ kPa}$$

Partial pressure of A in the mixture, $p_A = p_A^\circ \chi_A$

$$= 24 \times 0.6 = 14.4 \text{ kPa}$$

Partial pressure of B in the mixture, $p_B = p_B^\circ \chi_B$

$$= 12 \times 0.4$$

$$= 4.8 \text{ kPa}$$

Total pressure in the closed distillation apparatus

$$= p_A + p_B = 19.2 \text{ kPa}$$

Mole fraction of A in vapour state,

$$\chi'_A = \frac{p_A}{p_A + p_B} = \frac{14.4}{19.2} = 0.75$$

Mole fraction of B in vapour state,

$$\chi'_B = (1 - \chi'_A) = (1 - 0.75) = 0.25$$

The part $\chi'_A = 0.75$ is collected and redistilled. Hence, in second distillate,

p'_A = partial pressure of A = $p_A^\circ \chi'_A = 24 \times 0.75 = 18 \text{ kPa}$

p'_B = partial pressure of B = $p_B^\circ \chi'_B = 12 \times 0.25 = 3 \text{ kPa}$

Total pressure = $p'_A + p'_B = 18 + 3 = 21 \text{ kPa}$

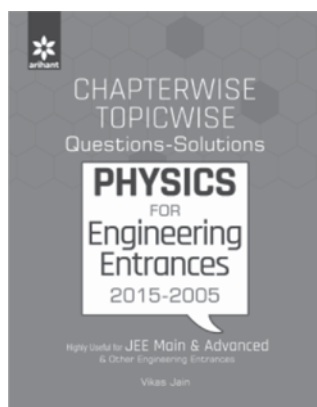
\therefore Mole fraction of A in second distillate

$$= \frac{p'_A}{p'_A + p'_B} = \frac{18}{21} = 0.857$$

\therefore Percentage of A in second distillate = 85.7%.

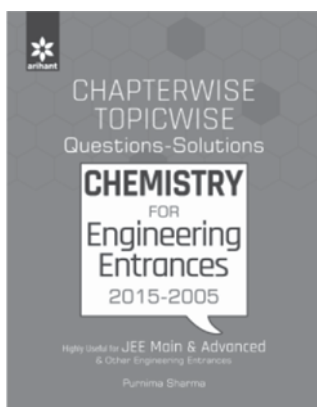
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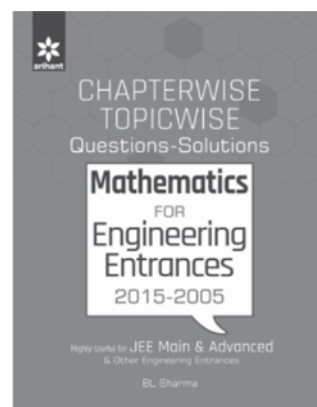
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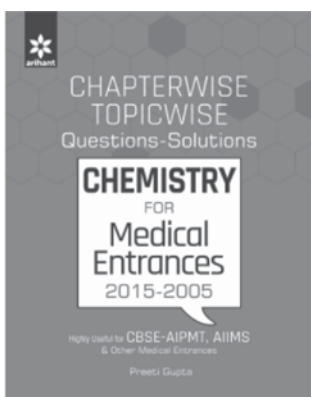
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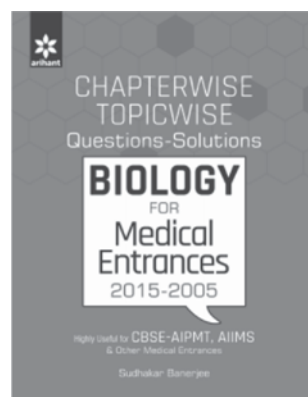
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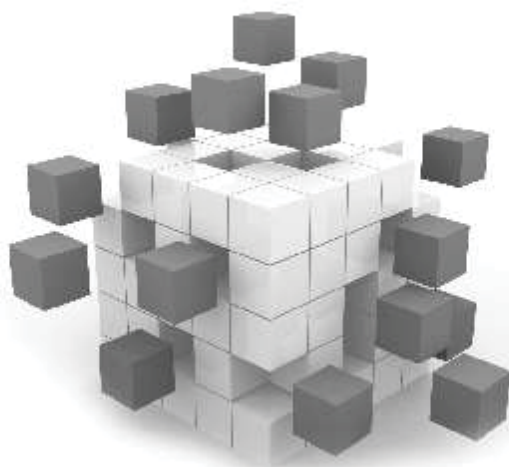
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30 BEST INTEGER TYPE PROBLEMS ON SOLID STATE



A collection of chapterwise best problems of their types

- Experimentally, it was found that a metal oxide has formula $M_{0.98}O$. The metal M is present as M^{2+} and M^{3+} in its oxide. The percentage of metal to the nearest integer that would exist as M^{3+} would be
- During the analysis of a sample of nickel oxide, it was found that the sample contains 96% nickel ions having d^8 configuration of $3d$ -orbitals and 4% having d^7 configuration of $3d$ -orbitals. If formula of compound is Ni_xO_y . Find the value of y .
- The crystal AB (rock salt structure) has molecular mass $6.023y$ u, where, y is an arbitrary number. If the minimum distance between the cation and anion is $y^{1/3}$ nm and the observed density is 20 kg m^{-3} , find the calculated density in kg m^{-3} .
- Silver (atomic mass = 108 g mol^{-1}) has a density of 10.5 g cm^{-3} . The number of silver atoms on a surface of area 10^{-12} m^2 can be expressed in scientific notation as $y \times 10^x$. The value of x is
- A compound AB has a rock salt structure with $A : B = 1 : 1$. The formula weight of AB is $6.023y$ u and the closest $A-B$ distance is $y^{1/3}$ nm. Calculate the density of the lattice in kg m^{-3} .
- The unit cell of silver iodide has four iodine atoms in it. How many silver atoms must be there in the unit cell?
- The density of CaO is 3.35 g/cm^3 . The oxide crystallises in one of the cubic system with an edge length of 4.80 \AA . How many Ca^{2+} and O^{2-} ions belong to each unit cell?
- A metal crystallises into two cubic systems face centred cubic (fcc) and body-centred cubic (bcc) whose unit cell lengths are 3.5 and 3.0 \AA , respectively. Calculate the ratio of densities of fcc to bcc to the nearest integer.
- Iron (II) oxide, FeO , crystal lattice has a cubic structure with edge length 5 \AA . Taking density of the oxide as 4.0 g cm^{-3} , calculate the number of Fe^{2+} and O^{2-} ions present in each unit cell.
- An organic compound crystallises in an orthorhombic system with two molecules per unit cell. The unit cell dimensions are 12.05 , 15.05 and 2.69 \AA . If the density of the crystal is 1.419 g cm^{-3} and molar mass is $x \times 10^{-1} \text{ kg mol}^{-1}$, find the value of x .
- A metallic element exists as a cubic lattice. Each edge of the unit cell is of 2.88 \AA . If the density of the metal is 7.20 g cm^{-3} and number of unit cell in 100 g of the metal is $x \times 10^{23}$, find the value of x to the nearest integer.
- At room temperature, polonium crystallises in primitive cubic unit cell. If $a = 3.36 \text{ \AA}$, molar mass of polonium = 209 g mol^{-1} and theoretical density of polonium is $9.15 \times 10^y \text{ kg m}^{-3}$, find the value of y .
- If the close packed cation in an AB type solid has a radius of 75 pm and maximum size of the anion filling the void is $x \times 10^2 \text{ pm}$, find the value of x .
- In LiI crystal, I^- ions form a cubical closest packed arrangement and Li^+ ions occupy octahedral holes. If the limiting radii of Li^+ is $x \times 10^{-13} \text{ m}$, find the value of x (edge length, $a = 600 \text{ pm}$).
- Barium crystallises in a body-centred cubic structure in which the cell-edge length is 0.5025 nm . If shortest distance between neighbouring barium atoms in the crystal is $2.17 \times 10^{-y} \text{ cm}$, find the value of y .
- A metallic element crystallises into a lattice containing a sequence of layers of $ABABAB\dots$ any packing of spheres leaves out voids in the lattice. If percentage by volume of this lattice is $(18 + x)\%$, find the value of x .

17. In a closed packed structure of mixed oxides, the lattice is composed of mixed oxide ions. One eighth of tetrahedral voids are occupied by divalent cations (A^{2+}) while one half of octahedral voids are occupied by trivalent cation (B^{3+}). If formula of mixed oxide is $A_xB_yO_z$, find the value of z .
18. An alloy of gold and copper, crystallises in a cubic lattice in which the gold atoms occupy the lattice points at the corners of a cube and the copper atoms occupy the centres of each of the cube faces. If the empirical formula of alloy is Au_xCu_y , find the value of y .
19. An element crystallises in fcc lattice having edge length 400 pm. If maximum diameter of atom which can be placed in interstitial site without distorting the structure is $x \times 10^{-10}$ m, find the value of x to the nearest integer.
20. The number of hexagonal faces that are present in a truncated octahedron is
21. Caesium bromide crystallises into a cubic system. Its unit cell has a Cs^+ ion at the body centre and a Br^- ion at each corner. Its density is 4.44 g cm^{-3} . Determine the edge length of the unit cell in \AA to the nearest integer value.
22. An element crystallises as body centred cubic lattice. Its density is 7.12 g cm^{-3} and the length of the side of the unit cell is 2.88 \AA . If the number of atoms present in 288g of the element is $x \times 10^{24}$. Find the value of x to the nearest integer value.
23. An element occurs in two crystalline forms α and β . The α -form has an fcc arrangement with $a = 3.68 \text{ \AA}$ and β -form has a bcc arrangement with $a = 2.92 \text{ \AA}$. Calculate the ratio of their densities.
24. In a compound, atoms of element Y form ccp lattice and those of element X occupy $2/3$ rd of tetrahedral voids. If formula of the compound is X_xY_y , find the value of x .
25. In a face-centred cubic lattice, atom A occupies the corner positions and atom B occupies the face-centre positions. If one atom of B is missing from one of the face-centred points, and formula of the compound becomes A_xB_y . Find the value of x .
26. In an orthorhombic lattice, the values of a , b and c are 4.2 \AA , 8.6 \AA and 8.3 \AA respectively. The molecular mass of the solute is given as 155 g mol^{-1} and its density is 3.3 g cm^{-3} , the number of formula units per unit cell is
27. A solid has a structure in which W atoms are located at the corners of cubic lattice, 'O' atoms at the centre of edges and Na atoms at the centre of the cube. If the formula of the compound is $Na_xW_yO_z$, find the value of x .
28. What is the mass (in g) of ideal crystal of NaCl, that contains 2.57×10^{21} unit cells?
29. A compound forms hexagonal close-packed structure. If the total number of voids in 0.5 mole of it is $x \times 10^{23}$, find the value of x .
30. The edge length of unit cell of a metal having molecular weight 75 g mol^{-1} is 5 \AA which crystallises in cubic lattice. If the density is 2 g/cc and radius of metal atom is $x \times 10^{-10}$ m, find the value of x .

Answers with Explanation

1. (4) As molecular formula of the metal oxide is $M_{0.98}O$.
Hence, the fraction of M in the molecular formula = 0.98
Let the fraction of M in oxidation state $M^{3+} = x$
 \therefore The fraction of M in oxidation state $M^{2+} = 0.98 - x$
Applying the law of electrical neutrality,
Total positive charge of metal ion = Total negative charge of oxide ion
 $\Rightarrow 3 \times x$ (due to M^{3+}) + $2 \times (0.98 - x)$ (due to M^{2+})
 $= 2 \times 1$ (due to O^{2-})
 $\Rightarrow x + 1.96 = 2$
or $x = 0.04$
 \therefore Percentage of M in +3 oxidation state
 $= \frac{0.04}{0.98} \times 100$
 $= 4.08\% \approx 4\%$
2. (1) The valence shell electronic configuration of Ni is
 Ni (28 electrons), $= 3d^8 4s^2$
 $\therefore Ni^{2+}$ (26 electrons), $= 3d^8$ and Ni^{3+} (25 electrons), $= 3d^7$
Hence, percentage of $Ni^{2+} = 96\%$, percentage of $Ni^{3+} = 4\%$
Let the number of O^{2-} ions present in the crystal = y
Applying the law of electroneutrality to the oxides of nickel,
Total positive charge due to nickel ions
 $=$ Total negative charge due to O^{2-} ions
 0.96×2 (due to Ni^{2+}) + 0.04×3 (due to Ni^{3+})
 $= y \times 2$ (due to O^{2-})
 $\Rightarrow 1.92 + 0.12 = 2$
 $\Rightarrow y = \frac{2.04}{2} = 1.02$
Hence, the formula of the crystal lattice is $Ni_{1.00}O_{1.02}$ or $Ni_{0.98}O_1$.

 JEE ADVANCED DRILL

3. (5) Density of the crystal AB can be calculated as

$$\rho = \frac{Z_{\text{eff}} \times M}{N_A \times a^3}$$

Since, AB has rock salt structure, $Z_{\text{eff}} = 4$

Edge length, $a = 2(r^+ + r^-) = 2y^{1/3} \text{ nm} = 2y^{1/3} \times 10^{-9} \text{ m}$

Molecular mass, $M_m = 6.023y \text{ g}$
 $= 6.023y \times 10^{-3} \text{ kg}$

$$N_A = 6.023 \times 10^{23}$$

$$\text{Hence, } \rho = \frac{4 \times 6.023y \times 10^{-3} \text{ kg}}{(2y^{1/3} \times 10^{-9} \text{ m})^3 \times 6.023 \times 10^{23}}$$

$$= 5.0 \text{ kg m}^{-3}$$

Hence, the calculated density of the crystal AB is $= 5.0 \text{ kg m}^{-3}$.

4. (7) Silver crystallises in fcc unit cell. Hence, number of Ag atoms per unit cell = 4

Let the edge length of unit cell = a

$$\rho = \frac{Z_{\text{eff}} \times M}{N_A \times a^3} = \frac{4 \times 108}{6.023 \times 10^{23} \times a^3}$$

$$= 10.5 \text{ g cm}^{-3} \text{ (Given)}$$

$$\Rightarrow a = 4 \times 10^{-8} \text{ cm} = 4 \times 10^{-10} \text{ m}$$

Now, surface area of unit cell

$$a^2 = (4 \times 10^{-10} \text{ m})^2$$

$$= 1.6 \times 10^{-19} \text{ m}^2$$

Number of unit cells on 10^{-12} m^2 surface area

$$= \frac{10^{-12}}{1.6 \times 10^{-19}} = 6.25 \times 10^6$$

\therefore There are two atoms (effectively) on one face of unit cell.

\therefore Number of atoms on 10^{-12} m^2 surface area

$$= 2 \times \text{number of unit cell}$$

$$= 2 \times 6.25 \times 10^6$$

$$= 1.25 \times 10^7$$

$$\Rightarrow x = 7$$

5. (5) Since, AB has rock salt arrangement, B^- ions will have fcc arrangement and A^+ ions occupy all the octahedral voids. Hence, there will be $4A^+$ and $4B^-$ ions per unit cell.

$$\therefore Z_{\text{eff}} = 4$$

Also for fcc arrangement,

$$r^- = \frac{a}{2\sqrt{2}} \quad \dots (i)$$

and for octahedral void

$$\frac{r^+}{r^-} = 0.414 = (\sqrt{2} - 1) \quad \dots (ii)$$

From Eqs. (i) and Eq (ii), we get

$$a = 2(r^+ + r^-)$$

$$= 2 \times y^{1/3} \times 10^{-9} \text{ m}$$

$[\therefore \text{closest } A - B \text{ distance} = y^{1/3} \text{ nm}]$

Also given $M_{AB} = 6.023y$

Now, density of AB crystal can be calculated as

$$\rho = \frac{Z_{\text{eff}} \times M}{N_A \times a^3}$$

$$= \frac{4 \times 6.023y \times 10^{-3} \text{ kg}}{6.023 \times 10^{23} \times (2y^{1/3} \times 10^{-9} \text{ m})^3} = 5.0 \text{ kg m}^{-3}$$

6. (4) The formula, AgI tells us that the ratio of silver atoms to iodine atoms is 1 : 1. Hence, if there are four iodine atoms in the unit cell, there must be four silver atoms.

$$7. (8) \rho (\text{density}) = \frac{n \times M}{a^3 \times N_A}$$

M of $CaO = (40 + 16) \text{ g} = 56 \text{ g}$ of CaO

n = number of molecules per unit cell

$$a = 4.80 \text{ \AA} = 4.80 \times 10^{-8} \text{ cm}$$

$$\rho = 3.35 \text{ g cm}^{-3}$$

$$n = \frac{3.35 \times (4.8 \times 10^{-8})^3 \times 6.023 \times 10^{23}}{56} = 3.98$$

$$\text{or } n \approx 4$$

So, 4 molecules of CaO are present in one unit cell.

\therefore Number of Ca^{2+} ions per unit cell = 4

Number of O^{2-} ions per unit cell = 4

\therefore Total Ca^{2+} and O^{2-} ions per unit cell = 8

8. (1) fcc unit cell length = 3.5 \AA

bcc unit cell length = 3.0 \AA

$$\text{Density for fcc } (\rho_{\text{fcc}}) = \frac{n_1 \times \text{atomic weight}}{V_1 \times N_A}$$

$$\text{Density for bcc } (\rho_{\text{bcc}}) = \frac{n_2 \times \text{atomic weight}}{V_2 \times N_A}$$

$$\therefore \frac{\rho_{\text{fcc}}}{\rho_{\text{bcc}}} = \frac{V_2 \times n_1}{V_1 \times n_2}$$

$$\text{For fcc, } n_1 = 4, V_1 = (3.5 \times 10^{-8})^3 \text{ cm}^3$$

$$[\therefore V = a^3]$$

$$\text{For bcc, } n_2 = 2, V_2 = (3.0 \times 10^{-8})^3 \text{ cm}^3$$

$$\therefore \frac{\rho_{\text{fcc}}}{\rho_{\text{bcc}}} = 1.259 \approx 1$$

9. (8) Volume of the unit cell

$$= (5 \times 10^{-10} \text{ m})^3 = 1.25 \times 10^{-28} \text{ m}^3$$

Density of $FeO = 4.0 \times 10^3 \text{ kg m}^{-3}$

$$\text{Mass of unit cell} = 1.25 \times 10^{-28} \text{ m}^3 \times 4.0 \times 10^3 \text{ kg m}^{-3}$$

$$= 5.0 \times 10^{-25} \text{ kg}$$

$$\text{Mass of one molecule of } FeO = \frac{\text{Molar mass}}{\text{Avogadro's number}}$$

$$= \frac{72 \times 10^3 \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$= 1.195 \times 10^{-25} \text{ kg}$$

\therefore Number of FeO molecules per unit cell

$$= \frac{5.0 \times 10^{-25} \text{ kg}}{1.195 \times 10^{-25} \text{ kg}}$$

$$= 4.18$$

$$\approx 4$$

Thus, there are four Fe^{2+} ions and four O^{2-} ions in each unit cell.

10. (2) Molar mass

$$= \frac{\text{Density} \times \text{Avogadro's number} \times \text{Volume}}{Z_{\text{eff}}}$$

$$= \frac{(1.419 \times 10^3 \text{ kg m}^{-3})(6.022 \times 10^{23} \text{ mol}^{-1})}{(12.05 \times 15.05 \times 2.69 \times 10^{-30} \text{ m}^3)}$$

$$= \frac{2}{2}$$

$$= 0.209 \text{ kg mol}^{-1}$$

or molar mass = $2.09 \times 10^{-1} \text{ kg mol}^{-1}$

$$\therefore x \approx 2$$

11. (6) Volume of the unit cell = $(2.88 \text{ \AA})^3 = 23.9 \times 10^{-30} \text{ m}^3$

$$\text{Volume of 100 g of the metal} = \frac{m}{\rho}$$

$$= \frac{0.1 \text{ kg}}{7.20 \times 10^3 \text{ kg m}^{-3}} = 13.9 \times 10^{-6} \text{ m}^3$$

\therefore Number of unit cells in this volume

$$= \frac{13.9 \times 10^{-6} \text{ m}^3}{23.9 \times 10^{-30} \text{ m}^3} = 5.82 \times 10^{23} \approx 6 \times 10^{23}$$

12. (3) A primitive cubic unit cell contains atoms only at the eight corners with each corner contributing $\frac{1}{8}$ th of the atom.

$$\text{Hence, } n = 8 \times \frac{1}{8} = 1$$

$$\text{Volume, } V = a^3 = (3.36 \text{ \AA})^3 = (3.36 \times 10^{-10} \text{ m})^3$$

$$\therefore \rho = \frac{Z_{\text{eff}} \times M}{N_A \times V}$$

$$= \frac{1 \times (209 \times 10^{-3} \text{ kg mol}^{-1})}{(6.022 \times 10^{23} \text{ mol}^{-1})(3.36 \times 10^{-10} \text{ m})^3}$$

$$= 9.15 \times 10^3 \text{ kg m}^{-3}$$

$$\therefore y = 3$$

13. (2) For close packed AB type solid,

$$\frac{r^+}{r^-} = 0.414 - 0.734$$

$$\therefore \text{Maximum value of } r^- = \frac{r^+}{0.414} = \frac{75}{0.414}$$

$$= 181.2 \text{ pm} = 1.81 \times 10^2 \text{ pm}$$

$$\therefore x \approx 2$$

14. (9) $2r^+ + 2r^- = 600 \text{ pm}$

$$r^+ + r^- = 300 \text{ pm} \quad \dots(i)$$

Since, Li^+ ions occupy octahedral holes, so for octahedral hole,

$$\frac{r^+}{r^-} = 0.414 \quad \dots(ii)$$

From Eq. (i) and Eq. (ii), we get

$$r^- \left(\frac{r^+}{r^-} + 1 \right) = 300$$

$$\text{or } r^- \times (0.414 + 1) = 300$$

$$\text{or } r^- = \frac{300}{1.414} = 212.164$$

$$\therefore r^+ = 212.164 \times 0.414$$

$$= 87.84 \text{ pm} = 8.7 \times 10^{-13} \text{ m}$$

$$\therefore x = 9$$

15. (8) For bcc lattice, diagonal = $\sqrt{3}a = 4r_{\text{Ba}}^+$

$$r_{\text{Ba}}^+ = \frac{\sqrt{3}}{4}a$$

$$r_{\text{Ba}}^+ = \frac{\sqrt{3}}{4} \times 0.5025 \times 10^{-7} \text{ cm}$$

$$= 2.176 \times 10^{-8} \text{ cm}$$

$$\therefore y = 8$$

16. (8) The arrangement ABABAB ... represents hexagonal close packed unit cell in which there are six atoms per unit cell. Also, volume of unit cell = $24\sqrt{2}r^3$.

$$\text{Packing fraction} = \frac{\text{Volume occupied by atoms}}{\text{Volume of unit cell}}$$

$$= 6 \times \frac{4}{3} \pi r^3 \times \frac{1}{24\sqrt{2}r^3} = 0.74$$

Percentage of empty space

$$= 100(1 - 0.74) = 26\%$$

or (18 + 8)%

$$\text{Hence, } x = 8$$

17. (4) Number of tetrahedral voids per ion in the lattice = 2

$$\text{Number of } A^{2+} = \frac{1}{8} \times 2 = \frac{1}{4}$$

Number of octahedral voids per ion in the lattice = 1

$$\text{Number of } B^{3+} = \frac{1}{2} \times 1 = \frac{1}{2}$$

\therefore Formula of mixed oxide is $A_{1/4} B_{1/2} O$ or AB_2O_4

$$\therefore z = 4$$

18. (3) Number of Au atoms per unit cell = $8 \times \frac{1}{8} = 1$

$$\text{Number of Cu atoms per unit cell} = 6 \times \frac{1}{2} = 3$$

Thus, formula of alloy is AuCu_3 .

$$\text{or } y = 3$$

19. (1) For a cubic system, there are two types of voids known as octahedral and tetrahedral voids. If r_1 is the radius of void and r_2 is the radius of atom creating these voids, then

$$\left(\frac{r_1}{r_2} \right)_{\text{octahedral}} = 0.414$$

$$\text{and } \left(\frac{r_1}{r_2} \right)_{\text{tetrahedral}} = 0.225$$

The above ratios show that octahedral voids has larger radius. Hence, for maximum diameter of atom, it should be present in octahedral void.

$$r_1 = 0.414r_2$$

Also for fcc, $4r_2 = \sqrt{2}a$

$$\therefore \text{Required diameter } (2r_1) = (2r_2) \times 0.414$$

$$= \frac{a}{\sqrt{2}} \times 0.414$$

$$= \frac{400 \times 0.414}{\sqrt{2}}$$

$$= 117 \text{ pm}$$

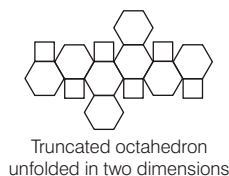
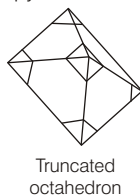
$$\text{or } = 1.17 \times 10^{-10} \text{ m}$$

$$\therefore x = 1$$

 JEE ADVANCED DRILL

- 20. (8)** The truncated octahedron is the 14-faced Archimedean solid: 6 squares and 8 regular hexagons.

The truncated octahedron is formed by removing the six right square pyramids one from each point of a regular octahedron as



- 21. (4)** The unit cell contains one Cs^+ and one Br^- .
Molecular mass (M) of $\text{CsBr} = 212.81 \text{ g mol}^{-1}$
Volume of cubic system (V) = $a^3 = \frac{\text{Mass of unit cell}}{\text{Density}}$

$$\text{or } a^3 = \frac{212.81 \times 1.66 \times 10^{-24}}{4.44} \text{ cm}^3 \quad [\because 1 \text{ u} = 1.66 \times 10^{-24} \text{ g}]$$

$$\text{or } a^3 = 79.7 \times 10^{-24} \text{ cm}^3 \text{ or } a = 4.30 \times 10^{-8} \text{ cm}$$

$$\text{or } a = 4.30 \times 10^{-10} \text{ m} = 4.30 \text{ \AA} \approx 4 \text{ \AA} \quad [\because 1 \text{ \AA} = 1 \times 10^{-10} \text{ m}]$$

- 22. (3)** Density (ρ) = $\frac{Z \times M}{a^3 \times N_A}$... (i)

Given, $\rho = 7.12 \text{ g cm}^{-3}$, $Z = 2$ (bcc lattice), $a = 2.88 \times 10^{-8} \text{ cm}$

$$N_A = 6.023 \times 10^{23}$$

$$\text{or } M = 51.2 \text{ g mol}^{-1} \quad [\text{from Eq. (i)}]$$

$$\therefore \text{Number of atoms in 288 g of element} = \frac{288}{51.2} \times 6.023 \times 10^{23}$$

$$= 3.39 \times 10^{24} \approx 3 \times 10^{24}$$

- 23. (1)** Z_{eff} for fcc = 4; Z_{eff} for bcc = 2

$$\text{Atomic volume of } \alpha\text{-form} = \frac{(3.68 \times 10^{-8})^3 \times N_A}{4}$$

$$\text{Atomic volume of } \beta\text{-form} = \frac{(2.92 \times 10^{-8})^3 \times N_A}{2}$$

[Atomic mass is same because element is same]

So, density ratio is

$$\rho_\alpha : \rho_\beta = V_\beta : V_\alpha = \frac{(2.92)^3}{2} : \frac{(3.68)^3}{4}$$

$$= 12.448 : 12.459 \approx 1 : 1$$

- 24. (4)** Suppose, atoms of element Y in ccp = 100

$$\text{Number of tetrahedral voids} = 2 \times 100 = 200$$

$$\text{Number of atoms of element X} = \frac{2}{3} \times 200 = \frac{400}{3}$$

$$\frac{X}{Y} = \frac{400}{300}$$

\therefore Formula of the compound will be X_4Y_3 .

$$\therefore x = 4$$

- 25. (2)** Number of atoms (A) per unit cell = $8 \times \frac{1}{8} = 1$

$$\text{Number of atoms (B) per unit cell} = (6 - 1) \times \frac{1}{2} = \frac{5}{2}$$

Thus, formula is $A_1B_{5/2} = A_2B_5$

$$\therefore x = 2$$

$$\begin{aligned} \text{26. (4)} \quad Z &= \frac{a^3 \times N_A \times \rho}{M} \\ &= \frac{4.2 \times 8.6 \times 8.3 \times 10^{-24} \times 6.023 \times 10^{23} \times 3.3}{155} \\ &= 3.84 \approx 4 \end{aligned}$$

$$\text{27. (1)} \quad \text{Number of W atoms per unit cell} = \frac{1}{8} \times 8 = 1 \text{ (At corners)}$$

$$\text{Number of oxygen atoms per unit cell} = \frac{1}{4} \times 12 = 3 \text{ (At edges)}$$

$$\text{Number of Na atoms per unit cell} = 1 \text{ (At centre)}$$

$$\therefore \text{W : O : Na} = 1 : 3 : 1$$

Hence, formula = NaWO_3

$$\therefore x = 1$$

- 28. (1)** Mass of one unit cell (m) = Volume \times density

$$= a^3 \times d$$

$$= a^3 \times \frac{MZ}{N_0 a^3}$$

$$\therefore \text{Mass of } 2.57 \times 10^{21} \text{ unit cells}$$

$$= 2.57 \times 10^{21} \times a^3 \times \frac{MZ}{N_0 a^3}$$

$$= \frac{2.57 \times 10^{21} \times 58.5 \times 4}{6.02 \times 10^{23}} \text{ g}$$

$$\approx 1 \text{ g}$$

- 29. (9)** Total number of atoms (N) in a closed packed structure (0.5 mol)

$$= 0.5 \times 6.023 \times 10^{23}$$

$$= 3.011 \times 10^{23}$$

$$\text{Number of octahedral voids (N)} = 3.011 \times 10^{23}$$

Number of tetrahedral voids

$$= 2N = 2 \times 3.011 \times 10^{23}$$

$$= 6.022 \times 10^{23}$$

Total number of voids

$$= 3.011 \times 10^{23} + 6.022 \times 10^{23}$$

$$= 9.033 \times 10^{23}$$

$$\text{or } x \approx 9$$

- 30. (2)** Number of atoms per unit cell

$$(Z) = \frac{\rho \times N_A \times a^3}{M}$$

$$= \frac{2 \text{ g cm}^{-3} \times 6.023 \times 10^{23} \text{ atoms mol}^{-1} \times (5 \times 10^{-8} \text{ cm})^3}{75 \text{ g mol}^{-1}}$$

$$= 2 \text{ (bcc)}$$

$$\text{For bcc, } 4r = \sqrt{3}a$$

$$\text{or } r = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \times 5 \times 10^{-10}$$

$$= 2.17 \times 10^{-10} \text{ m}$$

$$\text{or } \approx 2 \times 10^{-10} \text{ m}$$

$$\therefore x = 2$$

PERSONALITIES SPECTRUM



“SUCCESS IS NOT A PLACE AT WHICH ONE ARRIVES BUT RATHER THE SPIRIT WITH WHICH ONE UNDERTAKES AND CONTINUES THE JOURNEY”.

ALFRED BERNHARD NOBEL (21/10/1833-10/12/1896)

Alfred Nobel's greatness lay in his ability to combine the penetrating mind of the scientist and inventor with the forward-looking dynamism of the industrialist. Nobel was very interested in social and peace-related issues and held what were considered radical views in his era. He had a great interest in literature and wrote his own poetry and dramatic works. The Nobel Prizes became an extension and a fulfillment of his lifetime interests.

Nobel held 355 different patents among which, dynamite being the most famous one. After reading a premature obituary which condemned him for profiting from the sales of arms, he bequeathed his fortune to institute the **Nobel Prizes**. The synthetic element **nobelium** was named after him. His name also survives in modern-day companies such as **Dynamit Nobel** and **Akzo Nobel**, which are descendants of mergers with companies established by Nobel.

LIFE HISTORY

Alfred Nobel (1833-1896) was born in Stockholm, Sweden, on October 21, 1833. He was the third son of Immanuel Nobel (1801-1872), an inventor and an engineer, and Carolina Andriette (Ahlzell) Nobel (1805-1889). The couple married in 1827 and had eight children. The family was impoverished, and only Alfred and his three brothers survived from past childhood. Though his father, Alfred Nobel was a descendant of the Swedish scientist Olaus Rudbeck (1630-1702), and in his turn, the boy was interested in engineering, particularly explosives, learning the basic principles from his father at a young age. Alfred Nobel's interest in technology was inherited from his father, an alumnus of Royal Institute of Technology in Stockholm.

For 18 months, from 1841 to 1842, Nobel went to the only school he ever attended as a child, the Jacobs Apologistic School in Stockholm.

As a young man, Nobel studied with chemist Nikolai Zinin; then, in 1850, went to Paris to do further work. There he met Ascanio Sobrero, who had invented nitroglycerine three years before. Nitroglycerine was unpredictable, exploding when subjected to heat or pressure.

Nobel became interested in finding a way to control and use nitroglycerine as a commercially usable explosive, as it had much more power than gunpowder.

After the Nobel family's return to Sweden in 1863, Alfred concentrated on developing nitroglycerine as an explosive. Sadly, these experiments resulted in accidents that killed several people, including Alfred's younger brother, Emil. The government decided to ban these experiments within the Stockholm city limits. Alfred Nobel had to move his experimentation to a barge anchored on Lake Malaren. Alfred was not discouraged and in 1864, he was able to start mass production of nitroglycerine. To make the handling of nitroglycerine safer, Alfred Nobel done experiments with different additives.

Soon he found through his experiments, that mixing nitroglycerine with a fine sand called *kieselguhr* would turn the liquid into paste which could be shaped into rods. These rods could be inserted into drilling holes. The invention was made in 1866. Alfred got a patent or legal right of ownership on this material in the next year. He named it as "dynamite". He also invented a detonator or blasting cap which could be set off by lighting a fuse.

Accused of "high treason against France" for selling Ballistite to Italy, Nobel moved from Paris to Sanremo, Italy in 1891. On December 10, 1896 Alfred Nobel succumbed to a lingering heart ailment, suffered a stroke, and died. Unbeknownst to his family, friends or colleagues, he had left most of his wealth in trust, in order to fund the awards that would become known as the Nobel Prizes. He was buried in Norra begravningsplatsen in Stockholm.

CONTRIBUTION TO CHEMISTRY

Inventions of dynamite and detonator drastically reduced the cost of blasting rock, drilling tunnels, building canals and many other forms of construction work.

The market of dynamite and detonating caps grew very rapidly and Alfred Nobel also proved himself to be a very skillful entrepreneur and businessman. By 1865, his factory in Krummel near Hamburg, Germany, was exporting nitroglycerine explosives to other countries in Europe, America and Australia. Over the years, he founded factories and laboratories in some 90 different places in more than 20 countries. When he was not travelling or engaging in business activities, Nobel himself worked intensively in the various laboratories. He focused on the development of explosives technology as well as other chemical inventions.

Nobel, later on combined nitroglycerine with various nitrocellulose compounds, similar to collodion, but settled on a more efficient recipe combining another nitrate explosive, and obtained a transparent, jelly-like substance, which was a more powerful explosive than dynamite. 'Gelignite', or blasting gelatin, as it was named, was patented in 1876; and was followed by a host with similar combinations, modified by the addition of potassium nitrate and various other substances. Gelignite was more stable, transportable and conveniently formed to fit into bored holes, like those used in drilling and mining.

Alfred died in Sanremo, Italy, on December 10, 1896. In his last will and testament, he wrote that much of his fortune was to be used to give prizes to those who have done their best for humanity in the field of Physics, Chemistry, Physiology or Medicine, Literature and Peace.

In 1901, the first Nobel Prizes in Physics, Chemistry, Physiology or Medicine and Literature were awarded in Stockholm, Sweden and the Peace Prize in Kristiania (now Oslo), Norway.

EXEMPLAR SIMPLIFIED

EXTRACT OF EXTRA ORDINARY EXEMPLAR PROBLEMS

Solid State

Only One Correct Option Type Questions

- Which of the following is true about the value of refractive index of quartz glass?
(a) Same in all directions
(b) Different in different directions
(c) Cannot be measured
(d) Always zero
- Iodine molecules are held in the crystal lattice by
(a) London forces (b) dipole-dipole interactions
(c) covalent bonds (d) coulombic forces
- Which of the following solids is/are not electrical conductor(s)?
I. Mg(s) II. TiO(s)
III. I₂(s) IV. H₂O(s)
(a) Only I (b) Only II (c) III and IV (d) II, III and IV
- The lattice site in a pure crystal cannot be occupied by
(a) molecule (b) ion (c) electron (d) atom
- Which of the following point defects are shown by AgBr(s) crystal?
I. Schottky defect II. Frenkel defect
III. Metal excess defect IV. Metal deficiency defect
(a) I and II (b) III and IV (c) I and III (d) II and IV
- Which of the following statements is not true about the hexagonal close packing?
(a) The coordination number is 12
(b) It has 74% packing efficiency
(c) Tetrahedral voids of the second layer are covered by the spheres of the third layer
(d) In this arrangement, spheres of the fourth layer are exactly aligned with those of the first layer
- The percentage of empty space in a body-centred cubic arrangement is
(a) 74% (b) 68%
(c) 32% (d) 26%
- In which pair, most efficient packing is present?
(a) hcp and bcc (b) hcp and ccp
(c) bcc and ccp (d) bcc and simple cubic cell
- Which kind of defects are introduced by doping?
(a) Dislocation defect
(b) Schottky defect
(c) Frenkel defect
(d) Electronic defect
- Which of the following is not true about the ionic solids?
(a) Bigger ions form the close packed structure
(b) Smaller ions occupy either the tetrahedral or the octahedral voids depending upon their size
(c) Occupation of all the voids is not necessary
(d) The fraction of octahedral or tetrahedral voids occupied depend upon the radii of the ions occupying the voids
- In the cubic close packing, the unit cell has
(a) 4 tetrahedral voids each of which is shared by four adjacent units cells
(b) 4 tetrahedral voids within the unit cell
(c) 8 tetrahedral voids each of which is shared by four adjacent units cells
(d) 8 tetrahedral voids within the unit cell

Short Answer Type Questions

- In spite of long range order in the arrangement of particles, why are the crystals usually not perfect?
- Why does table salt, NaCl, sometimes appear yellow in colour?

14. Why is FeO(s) not formed in stoichiometric composition?
15. Why does white ZnO(s) become yellow upon heating?
16. In a compound, nitrogen (N) atoms make cubic close packed lattice and metal atoms (M) occupy one-third of the tetrahedral voids. Determine the formula of the compound formed by M and N?
17. Under which situations, can an amorphous substance change into crystalline form?

Matching Type Questions

18. Match the types of defect given in Column I with the statement given in Column II.

	Column I	Column II
A.	Impurity defect	p. NaCl with anionic sites called <i>F</i> -centres
B.	Metal excess defect	q. FeO with Fe ³⁺
C.	Metal deficiency defect	r. NaCl with Sr ²⁺ and some vacant cationic sites

19. Match the items given in Column I with the items given in Column II.

	Column I	Column II
A.	Mg in solid state	p. <i>p</i> -type semiconductor
B.	MgCl ₂ in molten state	q. <i>n</i> -type semiconductor
C.	Silicon doped with phosphorus	r. Electrolytic conductor
D.	Germanium doped with boron	s. Electronic conductor

Assertion and Reason Type

In the Following questions a statement of Assertion (A) followed by statement of Reason (R) is given. Choose the correct answer out of the following choices.

- (a) Assertion and Reason both are correct statements and Reason is correct explanation for Assertion
- (b) Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion
- (c) Assertion is correct statement but Reason is statement
- (d) Assertion is incorrect statement but Reason is correct statement
20. **Assertion (A)** Total number of octahedral voids present in a unit cell of cubic close packing including the one that is present at the body-centred, is four.

Reason (R) Besides the body-centred, there is one octahedral void present at the centre of each of the six faces of the unit cell and each of which is shared between two adjacent unit cells.

21. **Assertion (A)** Semiconductors are solids with conductivities in the intermediate range from 10⁻⁶ - 10⁴ ohm⁻¹m⁻¹.

Reason (R) Intermediate conductivity in semiconductors is due to partially filled valence band.

Long Answer Type Questions

22. A sample of ferrous oxide has actual formula Fe_{0.93}O_{1.00}. In this sample, what fraction of metal ions are Fe²⁺ ions? What type of non-stoichiometric defect is present in this sample?
23. Show that in a cubic close packed structure, eight tetrahedral voids are present per unit cell.

Answers with Explanation

1. (a) **Key Concept** Refractive index (*n*) of a material is a dimensionless number that describes how light propagates through that medium.

$$n = \frac{\text{Speed of light in vacuum}}{\text{Speed of light in the medium}}$$

Since, quartz glass is an amorphous solid having short range order of constituents. Hence, value of refractive index is same in all directions, can be measured and not always equal to zero.

2. (a) **Key Concept** London forces are
- weakest intermolecular forces.
 - temporary attractive forces that results when the electrons in two adjacent atoms occupy positions that make the atoms to form temporary dipoles.

Iodine molecules are a class of non-polar molecular solid in which constituent molecules are held together by London or dispersion forces. These solids are soft and non-conductor of electricity.

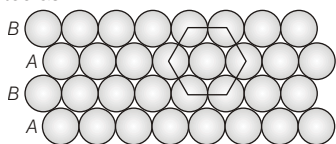
3. (c) Iodine is a non-polar molecular solid in which iodine molecules are held together by London or dispersion forces. It is soft and non-conductor of electricity.

Water is a hydrogen bonded molecular solid in which H and O are held together by polar covalent bond and each water molecule held together by hydrogen bonding. Due to non-ionic nature, they are not electrical conductor.

4. (c) Each point in a lattice is known as lattice point which is either atom or molecule or ion and joined together by a straight line to bring out geometry of lattice in pure crystal constituents. They are arranged in fixed stoichiometric ratio. Hence, existence of free electrons are not possible. It is possible only in case of imperfection in solid.
5. (a) In AgBr, both Ag⁺ and Br⁻ ions are absent from the lattice causing Schottky defect. However, Ag⁺ ions are mobile, so they have tendency to move aside the lattice and trapped in interstitial site, hence also shows Frenkel defect.

 EXTRA DOSE

6. (d) Hexagonal close packing can be arranged in two layers, i.e. A and B one over another which can be diagrammatically represented as



Here, we can easily see that 1st layer and 4th layer are not exactly aligned.

Thus, option (d) is not true while other statements (a), (b) and (c) are true.

7. (c) **Key Concept** Percentage of empty space = $100 - \text{packing efficiency}$

Packing efficiency for bcc arrangement is 68% which represents total filled space in the unit cell. Hence, empty space in body-centred arrangement is $100 - 68 = 32\%$.

8. (b) Packing efficiency is the percentage of total filled space by particles and it can be calculated as

$$\frac{\text{Volume occupied by four spheres in the unit cell}}{\text{Total volume of unit cell}} \times 100$$

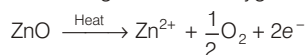
Since, packing efficiency for hcp and ccp is 74% which is maximum among all types of crystal.

9. (d) When electron rich or electron deficient impurity is added to a perfect crystal, it introduces electronic defect in them.
10. (d) The fraction of octahedral or tetrahedral voids occupied depend upon the radii of the ions present at the lattice points. As we know, the radius of octahedral or tetrahedral void is related to radius of atom (r) as
 Radius of octahedral void (R_o) = $0.414r$
 Radius of tetrahedral void (R_t) = $0.225r$
 where, r = radius of bigger atom involved
11. (d) In ccp lattice, the unit cell has eight tetrahedral voids. These voids are located slightly towards the centre from each corner of unit cell (1/4th way along the body diagonal). Hence, there are a total of eight tetrahedral voids, all located inside the unit cell.
12. The crystals have long range repeated pattern of arrangement of constituent particles. The reason of imperfection is due to the presence of impurity during the formation of a crystal.
13. Yellow colour in NaCl is due to metal excess defect due to which unpaired electrons occupy anionic sites, known as F -centres. These electrons absorb energy from the visible region for the excitation which makes crystal appears yellow.
14. FeO(s) is not formed in stoichiometric composition because of instability of FeO molecule. In FeO molecule, Fe^{2+} changes to Fe^{3+} by effectively replacing a small portion of Fe^{2+} with $\frac{2}{3}$ rd number of Fe^{3+} .

Thus, for every three missing Fe^{2+} ions, the crystal required two Fe^{3+} ions to balance the charge. This change in composition violates the law of constant composition of the compound. Thus, FeO becomes a non-stoichiometric compound.

15. **Key Concept** ZnO shows metal excess defect in which Zn^{2+} ions occupy the interstitial sites. Crystals that show such type of defects are generally coloured.

On heating, ZnO loses oxygen as follows:



Zn^{2+} ions and electrons move to interstitial sites and F -centres are formed which impart yellow colour to ZnO(s).

16. **Key Concept** Number of lattice points = Number of octahedral voids

Number of octahedral voids = $2 \times$ number of tetrahedral voids

Let the number of N atoms in ccp is x .

Number of tetrahedral voids = $2x$

$$\text{Number of } M \text{ atoms} = \frac{1}{3} \times 2x$$

$$\frac{\text{Number of } N \text{ atoms}}{\text{Number of } M \text{ atoms}} = \frac{3x}{2x} = \frac{3}{2}$$

So, the formula of the compound is M_2N_3 .

17. On heating, amorphous substance changes into crystalline form. Some objects from ancient civilisation are found to be milky in appearance. This is due to crystallisation.

18. $A \rightarrow r, B \rightarrow p, C \rightarrow q$

A. Impurity defect arises due to the addition of impurity ions having different charge than host ion.

B. Metal excess defect arises due to missing of cation from ideal ionic solid which leads to create a F -centre generally occupied by unpaired electron, e.g. NaCl with anionic site.

C. Metal deficiency defect arises due to missing of positive ion from the lattice site, e.g. In FeO, Fe^{3+} exists along with Fe^{2+} which lead to decrease in Fe^{2+} ion concentration so, this is a type of metal deficiency defect.

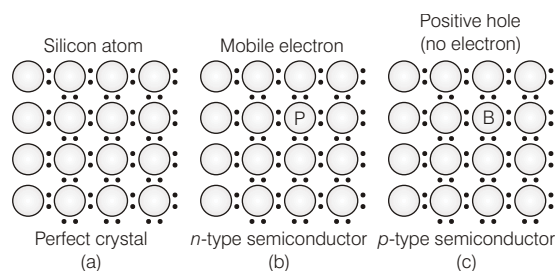
19. $A \rightarrow s, B \rightarrow r, C \rightarrow q, D \rightarrow p$

A. Mg in solid state shows electronic conductivity due to the presence of free electrons hence, it is known as electronic conductor.

B. MgCl_2 in molten state shows electrolytic conductivity due to the presence of electrolytes in molten state.

C. Silicon doped with phosphorus contains one extra electron due to which it shows conductivity under the influence of electric field and known as n -type semiconductor.

D. Germanium doped with boron contains one hole due to which it shows conductivity under the influence of electric field and known as p -type semiconductor.





- 20. (c) Key Concept** In ccp (fcc) lattice, species are present at six face centres and eight corners while octahedral voids are present at centre and twelve edge centres of the unit cell.

In ccp lattice, one complete octahedral void is situated at the centre of unit cell. Also, there are twelve octahedral voids with its centroid at the centre of edges of unit cell. Hence, these twelve octahedral voids are shared by four unit cells. Hence, total octahedral voids per unit cell in ccp is

$$= 1 + 12 \times \frac{1}{4} = 1 + 3 = 4$$

- 21. (c) Key Concept** Conductivity range

For conductors : $10^4 - 10^7 \text{ (in } \Omega^{-1}\text{m}^{-1}\text{)}$

For insulators : $10^{-20} - 10^{-10} \Omega^{-1}\text{m}^{-1}$

For semiconductor : $10^{-6} - 10^4 \Omega^{-1}\text{m}^{-1}$

Assertion is correct but Reason is incorrect statement. Semiconductors are solids with conductivities in the intermediate range varies from 10^{-6} to $10^4 \Omega^{-1}\text{m}^{-1}$. Intermediate conductivity is due to small energy gap between valence band and conduction band.

- 22. Plan** Consider the number of Fe^{2+} and Fe^{3+} ions as x and y respectively then write their sum equal to 0.93. Write another equation in terms of x and y by taking the sum of their total charge equal to 2 [charge on oxygen]. Now, using the substitution method, calculate the value of x and y then calculate fraction of Fe^{2+} ion present in this sample.

Let the formula of the sample be $(\text{Fe}^{2+})_x (\text{Fe}^{3+})_y \text{O}$.

On looking at the given formula of the compound,

$$x + y = 0.93 \quad \dots(i)$$

Total positive charge on ferrous and ferric ions should be balance the two units of negative charge on oxygen.

$$\text{Therefore, } 2x + 3y = 2 \quad \dots(ii)$$

$$\Rightarrow x + \frac{3}{2}y = 1 \quad \dots(iii)$$

On subtracting Eq. (i) from Eq. (iii), we get

$$\frac{3}{2}y - y = 1 - 0.93$$

$$\Rightarrow \frac{1}{2}y = 0.07$$

$$\Rightarrow y = 0.14$$

On putting the value of y in Eq. (i), we get

$$x + 0.14 = 0.93$$

$$\Rightarrow x = 0.93 - 0.14$$

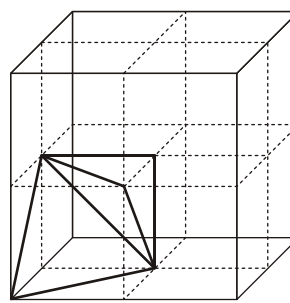
$$\Rightarrow x = 0.79$$

$$\text{Fraction of } \text{Fe}^{2+} \text{ ions present in the sample} = \frac{0.79}{0.93} = 0.849$$

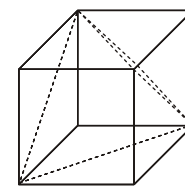
Metal deficiency defect is present in the sample because iron is less in amount than that required for stoichiometric composition.

- 23.** Cubic close packed structure contains one atom to each corner of unit cell and at face-centred of each unit cell. Each unit cell consists of 8 small cubes.

Each small cube contains 4 atoms at its alternate corner, when these atoms are joined to each other lead to creation of a tetrahedral void as shown below:



(a) Eight tetrahedral voids per unit cell of ccp structure



(b) One tetrahedral void showing the geometry

Since, there are total 8 smaller cubes present in one unit cell and each smaller cube has one tetrahedral void hence, total number of tetrahedral voids present in each unit cell is equal to eight.

As we know, ccp structure has 4 atoms per unit cell. Thus, total number of tetrahedral voids in one ccp unit cell is equal to 8.

CHEMISTRY IN action

Rare mixed-valent Si_2H radical isolated

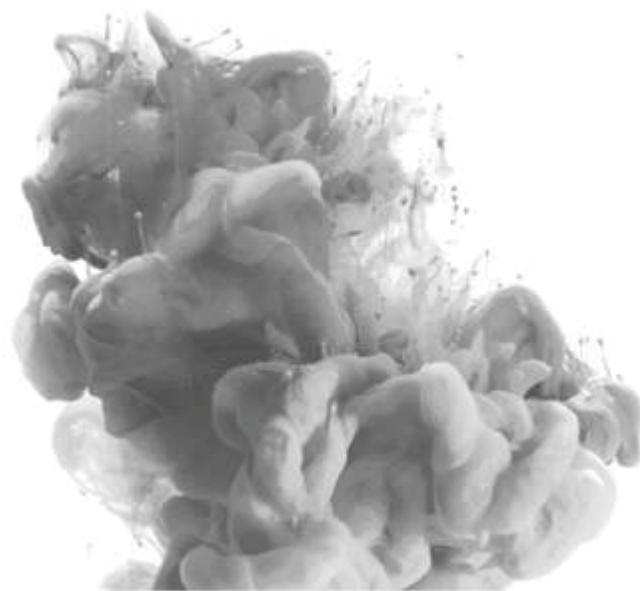
Scientists in Germany have isolated a disilicon hydride radical for the first time.

Open-shell silicon hydrides exist as transient species during chemical vapour deposition of silicon, a key process when making semiconductors for products such as solar cells. These compounds are very unstable and as a result are difficult to detect, let alone isolate. Scientists have now managed to trap a mixed-valent disilicon hydride radical between two N-heterocyclic carbenes. Theoretical and experimental investigations show that the unusual molecular fragment features a terminal silicon-hydrogen bond and asymmetric spin density across the silicon atoms.

The compound, which contains one silicon atom in the +1 oxidation state and the other in the 0 state, is remarkable as examples of isolated hydrides of silicon in oxidation states lower than +2 are very rare and open-shell congeners have never previously been reported. Following a one-electron reduction of a hydridodisilicon salt with potassium graphite the disilicon hydride radical was isolated as a dark green crystalline material that is stable at room temperature.

MOLE CONCEPT

FOR CLASS XI



Topicwise Collection of best subjective problems

Very Short Answer Type Questions [1 Mark]

- How many years it would take to spend one Avogadro's number of rupees at a rate of 10 lakhs of rupees in one second?
- A sample of He gas occupies 5.6 L volume at 1 atm and 273 K. How many mole of He are present in the sample?
- What will be the mass of 5 mole of SO_2 ?
- What is limiting reagent?
- The density of O_2 at 0°C and 1 atm is 1.42 g/L. Find the molar volume of the gas.
- Why Dulong-Petit method of determining atomic mass is not used often?
- How many moles of electron weighs 1 kg?
- At what conditions, Gay-Lussac's law of gaseous volume is not valid?
- If insulin contains 3.4% sulphur, what will be the minimum molecular mass of insulin?
- Why the actual yield in a reaction almost always less than the theoretical yield?

Short Answer Type Questions [2 Marks]

- Define the empirical formula. How would you determine the empirical formula of a compound?
- In the combustion of methane, what is the limiting reactant and why?
- Potassium chromate (K_2CrO_4) is isomorphous to potassium sulphate (K_2SO_4) and contains 26.78% chromium. Find the atomic mass of chromium. (atomic of K = 39.10)

- What do you understand by stoichiometric coefficients in a chemical equation?
- How many moles of magnesium phosphate, $\text{Mg}_3(\text{PO}_4)_2$ will contain 0.25 mole of oxygen atoms?

Short Answer Type Questions [3 Marks]

- When caffeine is burnt in excess of air, following products are obtained

$$2\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2 + 27\text{O}_2 \longrightarrow 16\text{CO}_2 + 10\text{H}_2\text{O} + 8\text{NO}_2$$
 Calculate the number of H_2O molecules formed when 19.4 g caffeine is burnt completely.
- The oxide of an element contains 32.33 per cent of the element and the vapour density of its chloride is 79. Calculate the atomic mass of the chloride.
- For the given reaction,

$$\text{CaO} + 2\text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O}$$
 1.23 g of CaO is reacted with excess of hydrochloric acid and 1.85 g of CaCl_2 is formed. What is the per cent yield?

Long Answer Type Questions [5 Marks]

- What do you understand by gram formula mass? If 20 g of CaCO_3 is treated with 20 g of HCl. How many grams of CO_2 is generated according to the following reaction?

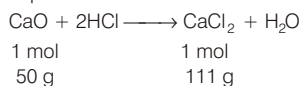
$$\text{CaCO}_3(g) + 2\text{HCl}(aq) \longrightarrow \text{CaCl}_2(aq) + \text{H}_2\text{O} + \text{CO}_2(g)$$
- A solid mixture (5.0 g) consisting of lead nitrate and sodium nitrate was heated below 600°C until the mass of the residue was constant. If the loss in mass is 28.0 per cent, find the amount of lead nitrate in the mixture.

Answers with Explanation

1. Number of rupees spent in one second = 10^6
 Number of rupees spent in one year
 $= 10^6 \times 60 \times 60 \times 24 \times 365$
 $= 3.15 \times 10^{13}$
 One Avogadro's number (6.023×10^{23}) of rupees will be spent
 $= \frac{6.023 \times 10^{23}}{3.15 \times 10^{13}} = 1.912 \times 10^{10} \text{ yr}$
2. Number of mole = $\frac{5.6}{22.4} = 0.25$
3. Molecular mass of $\text{SO}_2 = 64 \text{ g}$
 Number of moles = $\frac{\text{Mass(g)}}{\text{Molecular mass (g mol}^{-1}\text{)}}$
 $5 = \frac{\text{mass (g)}}{64}$
 Mass = 320 g
4. The reactant which gives the least amount of product on being completely consumed is called limiting reagent.
5. 1.42 g of O_2 gas occupies volume = 1 L
 $\therefore 32 \text{ g of O}_2 \text{ gas will occupy} = \frac{32}{1.42} = 22.4 \text{ L mol}^{-1}$
6. This method mainly determines atomic masses for metals and moreover, approximate values of atomic masses.
7. Mass of single electron = $9.108 \times 10^{-31} \text{ kg}$
 $\therefore 9.108 \times 10^{-31} \text{ kg} = \text{Mass of 1 electron}$
 $\therefore 1 \text{ kg} = \text{Mass of } \frac{1}{9.108 \times 10^{-31}} \text{ electron}$
 $= \frac{1}{9.108 \times 10^{-31}} \times \frac{1}{6.023 \times 10^{23}} \text{ moles of electrons}$
 $= \frac{10^8}{9.108 \times 6.023} \text{ moles of electrons}$
 $= 1.82 \times 10^6 \text{ moles of electrons}$
8. Gay-Lussac's law of gaseous volume is not valid when reactants and products are present in solid or liquid state.
9. For minimum molecular mass, insulin must contain atleast one sulphur atom in its one molecule.
 When 3.4 g sulphur is present then molecular mass of insulin = 100
 If 32 g sulphur is present, then molecular mass of insulin will be
 $= \frac{100 \times 32}{3.4} = 941.14$
10. Due to some side reactions taking place simultaneously.
11. **Empirical formula** It represents the simplest relative whole number ratio of atoms of each element present in the molecule of the substance.
 To get the empirical formula, symbols of various elements present are written side by side with their respective whole number ratio as a subscript to the lower right hand corner of the symbol.
12. In combustion of methane, the other reactant is oxygen from the air which is always present in excess. Thus, the amounts of CO_2 and H_2O formed will be depend upon the amount of CH_4 burnt. Limiting reactant can be decided only when amount of reactants available are known.
13. If the atomic mass of chromium is A, then for K_2CrO_4 ,
 $= 2 \times 39.1 + A + 64$
 $= (142.2 + A)$
 Percentage of chromium
 $= \frac{A}{(142.2 + A)} \times 100$
 So, $\frac{100 A}{(142.2 + A)} = 26.78$
 $100 A = 26.78 (142.2 + A)$
 $A = \frac{26.78 \times 142.2}{73.22}$
 $= 52.01$
14. The coefficients of reactants and products involved in a chemical equation represented by the balanced form, are known as stoichiometric coefficients.
 e.g. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$
 The stoichiometric coefficients of reactants and product in the above reaction are 1, 3 and 2 respectively.
 Stoichiometric coefficients represent the number of molecules (and moles as well) taking part in the reaction or formed in the reaction.
15. In $\text{Mg}_3(\text{PO}_4)_2$ molecule, 8 moles of O-atom are contained by 1 mole $\text{Mg}_3(\text{PO}_4)_2$.
 Hence, 0.25 mole of O-atom are contained by $\text{Mg}_3(\text{PO}_4)_2$
 $= \frac{1}{8} \times 0.25$
 $= 3.125 \times 10^{-2} \text{ mole}$
16. Moles of caffeine
 $= \frac{19.4}{194} = 0.1 \text{ mole}$
 According to chemical equation,
 2 moles of caffeine = 10 mole of H_2O
 \therefore Moles of water formed
 $= \frac{10}{2} \times 0.1 = 0.5 \text{ mole}$
 So, number of water molecules
 $= 0.5 \times 6.023 \times 10^{23}$
 $= 3.01 \times 10^{23}$
17. Mass of the element = 32.33 parts
 Mass of oxygen = $(100 - 32.33)$
 $= 67.67 \text{ parts}$
 Equivalent mass of the element
 $= \frac{32.33}{67.67} \times 8$
 $= 3.82$
 Valency of the element
 $= \frac{2 \times \text{Vapour density}}{E \times 35.5}$
 $= \frac{2 \times 79}{3.82 \times 35.5}$
 $= 1$

 TOUCH UP

18. The balanced equation



56 g of CaO produces $\text{CaCl}_2 = 111 \text{ g}$

1.23 g of CaO will produce CaCl_2

$$= \frac{111}{56} \times 1.23 = 2.43 \text{ g}$$

Thus, theoretical yield = 2.43 g

Actual yield = 1.85 g

$$\text{Per cent yield} = \frac{1.85}{2.43} \times 100 = 76.1\%$$

19. Mole of $\text{CaCO}_3 = \frac{20}{100} = 0.2$

$$\text{Mole of HCl} = \frac{20}{36.5} = 0.548$$

$$\frac{\text{Mole}}{\text{Stoichiometric coefficient}} \text{ for } \text{CaCO}_3$$

$$= \frac{0.2}{1} = 0.2$$

$$\frac{\text{mole}}{\text{stoichiometric coefficient}} \text{ for HCl}$$

$$= \frac{0.548}{2} = 0.274$$

So, CaCO_3 is limiting reagent.

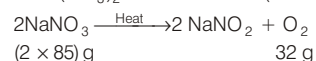
100 g of CaCO_3 gives 44 g of CO_2

$$\therefore 20 \text{ g of } \text{CaCO}_3 \text{ will give } \frac{44}{100} \times 20$$

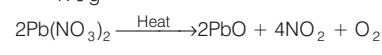
$$= 8.8 \text{ g } \text{CO}_2$$

20. Let the amount of NaNO_3 in the mixture be $x \text{ g}$.

\therefore The amount of $\text{Pb}(\text{NO}_3)_2$ in the mixture = $(5.0 - x) \text{ g}$



$$= 170 \text{ g}$$



$$(2 \times 331) \text{ g} \qquad \qquad \qquad (4 \times 46) \text{ g } 32 \text{ g}$$

$$662 \text{ g} \qquad \qquad \qquad 216 \text{ g}$$

170 g of NaNO_3 evolve oxygen = 32 g

$$x \text{ g of } \text{NaNO}_3 \text{ evolve oxygen} = \frac{32x}{170} \text{ g}$$

662 g of $\text{Pb}(\text{NO}_3)_2$ evolve NO_2 gas = 216 g

$(5.0 - x) \text{ g}$ of $\text{Pb}(\text{NO}_3)_2$ evolve gases

$$= \frac{216}{662} \times (5.0 - x) \text{ g}$$

Loss given in the problem

$$= \frac{28}{100} \times 5 = 1.4 \text{ g}$$

$$\therefore \text{Total loss} = \frac{32}{170} x + \frac{216}{662} \times (5.0 - x)$$

On solving, $x = 1.670 \text{ g}$

Thus, mass of $\text{NaNO}_3 = 1.670 \text{ g}$

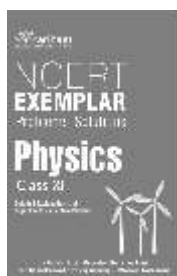
Mass of $\text{Pb}(\text{NO}_3)_2 = (5.0 - 1.676) \text{ g}$

$$= 3.324 \text{ g}$$

DETAILED SOLUTIONS

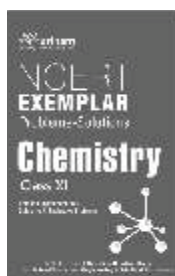
NCERT EXEMPLAR PROBLEMS

FOR CLASS XIth & XIIth



F259

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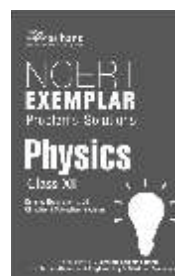
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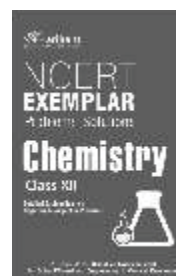
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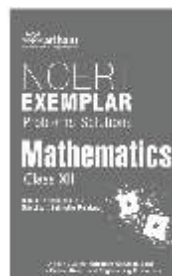
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DO YOU KNOW



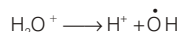
Amazing facts with proper explanation

▶ How radiation damages our tissues?

Highly energised radiation damages tissues by causing ionisation. That is, the radiation knocks electrons out of the molecules that make up the tissue, thereby forming unstable ions, e.g. the interaction of high energy radiation with water forms an unstable cation.



The positive charge on the H_2O^+ means that one of the electrons normally present in the water molecule, either in a covalent bond or an unshared pair, is missing in this cation, it has been knocked out. Once formed, the cation is unstable and decomposes.



The $\dot{\text{O}}\text{H}$ has an unpaired electron which makes it extremely reactive. These free radicals rapidly interact with other molecules, causing chemical reactions that damage the tissues. These reactions have serious consequences if they occur inside the cell nucleus and damage genetic material. In addition, they affect rapidly dividing cells more than the stationary cell. Thus, the damage is greater to embryonic cells, cells of the marrow and intestines, and cells in the lymph. Symptoms of radiation sickness include nausea, vomiting, a decrease in the white blood cell count and loss of hair.

▶ Sunglasses with adjustable shading follow Le Chatelier's principle.

The compound silver chloride is incorporated in the sunglasses with adjustable shading. This compound, on exposure to sunlight, produces metallic silver, Ag.



The more silver produced, the darker the glasses. At night, or when the wearer goes indoors, the reaction is reversed according to Le-Chatelier's principle. In this case, the addition of sunlight drives the equilibrium to the right, its removal drives it to the left.

▶ Molybdenum disulphide layer of less than 1 nm, can absorb more than 35% of incident light in the 400 to 700 nm wavelength range.

Generally, molybdenum disulphide (MoS_2) is used as a lubricant in aircraft and motorcycle engines. It is also used in the universal joints of trucks and automobiles. Isabell Thomann, a researcher of Rice University, knows it as a remarkably light-absorbent substance that holds promise for the development of energy-efficient upto electronic and photocatalytic devices.

Basically, it was based how much light can be confined in an atomically thin semiconductor monolayers of MoS_2 . It can be done by using simple strategies. It was found that a thin layer of MoS_2 which is only 0.7 nm thick, can absorb 35-37% of the incident light in the 400 to 700 nm wavelength range.

Thomann and her team used a combination of numerical simulations, analytical models and experimental optical characterisations. They found that using three-dimensional electromagnetic simulations, light absorption was enhanced 5.9 times compared with using MoS_2 on a sapphire substrate.

▶ Life of a lithium ion battery can be increased by two to three times with atomic layer deposition.

Lithium ion batteries are used in many daily usable objects such as laptops, computers, cellphones etc that need to be charged their batteries seemingly everyday.

Researchers solve this problem by using thin film coating technique called atomic layer deposition (ALD). This technique includes doping and coating lithium-magnesium-nickel-oxygen (LMNO) with iron oxides through ALD at the same time. Doping means adding an element or compound into the crystalline structure, or lattice, filling the gaps in the LMNO coating is what it sounds like, putting ultra-thin layer of iron oxide.

More important than the manufacturing aspect is the battery's ability to deliver a sustained performance over a long period of time, which is a big benefit to the consumer. By this technique, lithium ion battery gets 93% capacity retention after 1,000 cycles of charge and discharge at room temperature and 91% at elevated temperatures that is equivalent to about three years of battery life with almost same performance as of a new battery.

The coating process is carried out at 450°C under reduced pressure. The materials are placed inside a fluidised bed reactor, and vibrating motors shake the reactor to improve the mixing of particles and gaseous chemical. ALD has the potential to prepare these ultra-thin electrochemically active films with optimal thickness and synergetic effect of conductive coating and element doping, providing the industry with novel-design electrodes that are durable as well as functional at high temperature and fast cycling rates.

▶ It is more economical to fill a gas tank in the cool morning rather than in warm afternoon.

Can you imagine, you can reduce your automobile fuel bills by applying the density concept. The density of most liquids decreases as the temperature increases and *vice-versa*. Thus, density of gasoline decreases in the warm afternoon, and increases in the cold morning.

Gasoline is sold at the pump by the volume delivered (gallone), and not by the mass, which is greater when density increases. Although, 100 rupees of fuel contain the same volume at different temperature, 100 rupees of fuel contain a greater mass of gasoline at 15°C than at 35°C because the density increases with increase in temperature. Thus, filling up with gas in the cool morning saves money.

There are only two liquids that violate the principle of greater density at a lower temperature. These liquids are water and ammonia. At temperatures near their freezing points (0°C and -77°C, respectively), each of these liquids expands to form a crystalline solid. Consequently, the density of water decreases and solid ice demonstrates the unusual property of floating in water. Similarly, solid ammonia floats over liquid ammonia.

IMPERFECTIONS IN SOLIDS

FOR CLASS XII

Topicwise Collection of best subjective problems

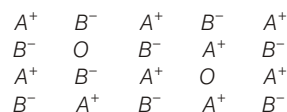


Very Short Answer Type Questions [1 Mark]

1. Define 'imperfection in solids'.
2. Which factors in solid are responsible for raising electronic imperfections?
3. When a substance is heated, which defect can be developed?
4. Why electrical neutrality is maintained in Schottky defects?
5. Why does AgBr show both Schottky and Frenkel defects?
6. White colour of zinc oxide at room temperature, this can be verified by which defect ?
7. Write two compounds which can show metal deficiency defect.
8. Name the defect which is also known as dislocation defect.
9. What happens to electrical conductivity when Ag^+ in AgBr is dislocated from its original site?
10. Why is Frenkel defect not found in pure alkali metal halides?

Short Answer Type Questions [2 Marks]

11. LiCl appears pink in colour when heated in Li vapours. Explain.
12. Define the terms.
(i) Non-stoichiometric defect (ii) Interstitial defect
13. Write down the formulae for the following
(i) The number of Schottky defects present in an ionic crystal containing N ions at temperature ' T '.
(ii) Number of impurity defects per cm^3 .
14. Examine the given defective crystal.



Answer the following questions.

- (i) What type of stoichiometric defect is shown by the crystal?
 - (ii) How is the density of the crystal affected by this defect?
15. Calcium crystallises in fcc unit cell with 0.556 nm edge length. Calculate the density if it contains 0.2% Frenkel defects.

Short Answer Type Questions [3 Marks]

16. Explain the following
(i) The addition of CaCl_2 crystal to a KCl crystal lowers the density of the KCl crystal.
(ii) Group-13 elements have more electrical conductivity than group-14 elements.
17. Calcium crystallises in fcc unit cell with 0.5 nm edge length. Calculate the density if it contains 0.1% Schottky defects.
18. Write down any two affects of the following on the crystal.
(i) Schottky defect
(ii) Frenkel defect

Long Answer Type Questions [5 Marks]

19. If NaCl is doped with 10^{-3} mol% GaCl_3 then calculate the total number of cation vacancies per mole of NaCl.
20. Justify the following sentences.
(i) Schottky defect appears more common than Frenkel defect.
(ii) The crystals with metal excess defects are generally coloured.
(iii) Crystal of germanium has very low electrical conductance.
(iv) ZnS shows Frenkel defect.
(v) NaCl shows Schottky defect.

Answers with Explanation

1. Any departure from perfectly ordered arrangement of atoms in a crystal is known as 'imperfection in solids'.
2. The electrons and holes in solids are responsible to rise electronic imperfections.
3. Vacancy defect can be developed, when a substance is heated.
4. Electrical neutrality is maintained in Schottky defects due to disappearance of same number of cations and anions from their lattice sites.
5. AgBr shows both Schottky and Frenkel defects because AgBr is highly ionic but there is a larger difference in the size of Ag^{\oplus} and Br^{\ominus} .
6. Colour appears due to F -centres which is a part of metal excess defects.
7. FeO, NiO
8. Frenkel defect which is a stoichiometric defect, is also known as dislocation defect.
9. When Ag^+ in AgBr is dislocated from its normal site to an interstitial site, electrical conductivity increases to a smaller extent.
10. Alkali metal halides have similar size of cations and anions, thus Frenkel defect is not shown by these halides.
11. The Cl^- ions diffuse to the surface where they combine with Li^+ and form LiCl. An electron is released which diffuses into the crystal and occupies the anionic site. The pink colour results by the excitation of the electrons when they absorb energy from visible light falling on the crystal.
12. (i) **Non-stoichiometric defect** The imperfection arises when ratio of cations to anions differs from that indicated by their molecular formula. Then, the defect is known as non-stoichiometric defect. These defects result in either excess of metal or non-metal atom.
(ii) **Interstitial defect** When some constituent particles, i.e. atoms or molecules occupy an interstitial site, the crystal is said to have interstitial defect.
13. (i) Number of Schottky defects (n) present in an ionic crystal containing N ions at temperature T is written as,

$$n = Ne^{-E/2kT}$$
 where,
 E = Energy required to create n Schottky defects
 K = Boltzmann constant
 (ii) Number of impurity defects per cm^3 is given as,

$$n' = N' \times e^{-W/2RT}$$
 where, N' = number of sites per cm^3
 W = Work or energy required to produce defect
 T = Absolute temperature
 R = Gas constant
 e = Base of natural logarithm
14. (i) Schottky defect is shown by the given crystal.
(ii) Due to this defect, density of crystal decreases.
15. Frenkel defects do not change the theoretical value of the density because the atom is occupying an interstitial position instead of a lattice position.
16. (i) Since, one Ca^{2+} and two K^+ leave the crystal to maintain the electrical neutrality of the compound. The mass of two K^+ is greater than the mass of one Ca^{2+} . Hence, the density of the crystal decreases.
(ii) Since, group-13 elements have one valence electron less than group-14 elements leading to electron-deficient bond or hole. Such holes can move across the crystal giving rise to electrical conductivity of group-13 elements.
17. Z_{eff} of Ca = 4 atoms per unit cell (in fcc)
 \therefore There are 0.1% Schottky defects

$$\therefore Z_{\text{eff}} = \left(4 - \frac{0.1}{100} \times 4\right) = 3.996$$

$$\rho = \frac{Z_{\text{eff}} \times M}{N_A \times a^3}$$

$$= \frac{3.996 \times 40 \text{ g}}{(6 \times 10^{23} \text{ mol}^{-1})(0.5 \times 10^{-7} \text{ cm})^3}$$

$$= 2.131 \text{ g cm}^{-3} \quad (\because 1 \text{ nm} = 10^{-9} \text{ m} = 10^{-7} \text{ cm})$$
18. (i) The two effects of Schottky defect are as follows:
(a) The number of ions in these defects decreases but volume remains same, so the density decreases.
(b) Due to the presence of holes or unoccupied sites in the crystal, the stability or lattice energy of the crystal decreases.
(ii) The two effects of Frenkel defect are as follows:
(a) The electrical conductivity of a solid decreases.
(b) The dielectric constant of the crystal increases.
19. 100 mol of NaCl are doped with 10^{-3} mol of GaCl_3 .
 \therefore 1 mol of NaCl is doped with $\text{GaCl}_3 = \frac{10^{-3}}{100} = 10^{-5}$ mol
 As to introduce one Ga^{3+} ion, three Na^+ have to be removed to maintain the electrical neutrality. So, as one vacancy is filled by Ga^{3+} , two cation vacancies are formed.
 \therefore Concentration of cation vacancy
 $= 2 \times 10^{-5}$ mol of NaCl
 $= 2 \times 10^{-5} \times 6.023 \times 10^{23} \text{ mol}^{-1}$
 $= 12.046 \times 10^{-18} \text{ mol}^{-1}$
 $= 1.2046 \times 10^{-19} \text{ mol}^{-1}$
20. (i) Because the energy required for a Schottky defect is much less than that required for a Frenkel defect.
(ii) Due to the presence of free electrons, which get excited easily from lower to higher energy level by absorption of certain wavelength of light. Therefore, compounds appear coloured.
(iii) Ge has four electrons in the outer shell which is available for bonding. Since, there is no free electrons hence, electrical conductance is low for crystal of Ge.
(iv) In ZnS crystal, Zn^{2+} ions are trapped in the interstitial space leaving holes in the lattice and therefore shows Frenkel defect.
(v) Schottky defects appear in strongly ionic compounds with high coordination number and in which radius ratio is not far below unity. In NaCl, coordination number is 6 : 6 and it is an ionic compound as well. Hence, it shows Schottky defect.



CHEMISTRY @ SPECTRUM FOR YOU



In this section, we invite our readers to send their problems and we will try to provide the best possible solutions given by our expert panel.



Dear Sir, I heard a lot about diabetes and severe complications like blindness, loss of an arm or leg etc.

because of it. How diabetes affects the health of a person and what are the causes of it?

[Ajay Kumar, Meerut]

- Dear Ajay, diabetes is a disorder of metabolism in which the body cannot produce or produces low hormone insulin. In a normal person, the pancreas, a large gland behind stomach, secretes insulin and other hormones. Our body converts most of the food we eat into glucose. Insulin is necessary for glucose molecules to penetrate such cells as brain, muscle, and fat cells, where they can be used. One signal that a person is diabetic is that the concentration of glucose in his or her blood is higher (600 mg/100 mL) than the normal (80 to 100 mg/100 mL):

There are two kinds of diabetes:

Type I Insulin dependent diabetes

In this, the patients do not produce enough of insulin in the pancreas. This type of diabetes is treated by daily injecting insulin to the patient and it develops early, before the age of 20.

Even with daily injections of insulin, the blood sugar level fluctuates, which may cause other disorders such as retinal dystrophy leading to blindness, kidney disease, heart attack and nervous disorders.

Type II Non-insulin dependent diabetes

In this, the patient has enough insulin in the blood but cannot utilise it properly. This type of diabetes develops after the age 40. Overweight people usually suffer with this type of diabetes. Oral drugs can help in this type of diabetes.

Usually for measurement of glucose level in the blood, a prick of the finger is introduced onto a small strip of paper that contains numerous chemicals that react specifically with glucose. Insertion of the strip into a small battery operator reader gives the glucose concentration value.



Dear Sir, how can I do calculations which involves many variables for state of

matter topic?

[Isha, Muzaffarnagar]

- Isha, in states of matter topic, you encounter a variety of problems based on the ideal gas equation, which consists of four experimental quantities- p , V , n and T . To avoid any difficulty, you may go through the following steps:

Step I Tabulate information

Read the problems carefully to determine which quantity is unknown and which are given.

Step II Convert to consistent units

Make certain that quantities are converted to the proper units by using the correct conversion factors.

e.g. R has the units J/mol-K. If you are given a pressure in atm, you will need to convert it into Nm^{-2} .

Step III If a single equation relates the variables, rearrange the equation to solve for the unknown,

e.g.
$$p = \frac{nRT}{V}; V = \frac{nRT}{p}; n = \frac{pV}{RT}; T = \frac{pV}{nR}$$

Step IV Use dimensional analysis

If the units of the quantities in the equation cancel properly to give the units of the desired variable, you have used the equation correctly.

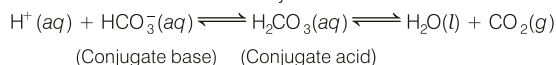
Step V Sometimes, the necessary variables are not given directly. Rather, values of other quantities that can be used to determine the desired variable, are given. Thus, desired variable can be obtained by solving the other quantities.

Q3 Dear Sir, our blood maintains a specific pH range (7.35 to 7.45) and behaves as a buffer solution. If this pH range is disturbed to a higher or lower level, what will happen to our body? **[Aarti, Dehradun]**

- Aarti, you have asked a very interesting question. Human blood maintains normal pH of 7.35 to 7.45 which is slightly basic. Any deviation from this normal pH range can have extremely disruptive effects on the stability of cell membranes, the structure of proteins and activities of enzymes.

Death may result if the pH of blood falls below 6.8 or rises above 7.8. When the pH falls below 7.35, the condition is called *acidosis* and when it rises above 7.45, the condition is called *alkalosis*. Acidosis is the more common tendency because ordinary metabolism generates several acids within the body.

The major buffer system that is used to control the pH of blood is the carbonic acid bicarbonate buffer system.



Although, carbonic acid is a diprotic acid, the carbonate ion (CO_3^{2-}) is not important in this system. CO_2 is the component of above equilibrium and is a gas, which provides a mechanism for the body to adjust the equilibrium. Removal of CO_2 via exhalation shifts the equilibria to the right, consuming H^+ ions. The buffer system in blood operates at a pH of 7.4, which is fairly removed from the $\text{p}K_{\text{a1}}$ value of

H_2CO_3 (6.1 at physiological temperature). For the buffer to have a pH of 7.4, the ratio $\frac{[\text{base}]}{[\text{acid}]}$ must have a value of about 20. In normal blood

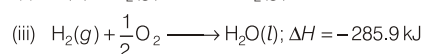
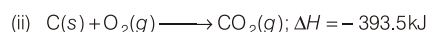
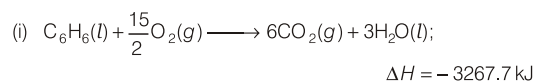
plasma, the concentrations of HCO_3^- and H_2CO_3 are about 0.024 M and 0.0012 M, respectively. Consequently, the buffer has a high capacity to neutralise additional acid, but only a low capacity to neutralise additional base.

Q4 Dear Sir, Hess's law is used for calculation of lattice enthalpy of NaCl or KCl. Can we not use this law for the calculation of enthalpies for other compounds? **[Aakash, Pune]**

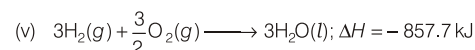
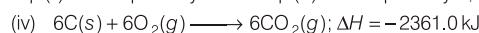
- Dear Aakash, Hess's law is not limited to calculate lattice enthalpy of NaCl or KCl only. But it has wide applications in calculation of enthalpies of formation of many compounds. There are many compounds whose enthalpies are calculated by the application of Hess's law when it is not possible to determine these experimentally.

For example, it is impossible to determine experimentally the enthalpy of formation of benzene from its elements: carbon and hydrogen. However, it can be calculated from the enthalpy of combustion of benzene and the enthalpies of formation of water and carbon dioxide. The solution is carried out in two steps:

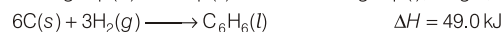
Step I The thermochemical equations for the known values are written as



Step II Eq. (ii) is multiplied by 6 and Eq. (iii) is multiplied by 3, we get



Adding Eq. (iv) and Eq. (v) and subtracting Eq. (i), we get,



Thus, the enthalpy of formation of benzene is + 49.0 kJ.

CHEMISTRY IN action

The most earth-abundant resource, seawater, is utilized to produce a solar fuel that is H_2O_2

Scientists have used sunlight to turn seawater (H_2O) into hydrogen peroxide (H_2O_2), which can then be used in fuel cells to generate electricity. It is the first photocatalytic method of H_2O_2 production that achieves a high enough efficiency so that the H_2O_2 can be used in a fuel cell. The biggest advantage of using liquid H_2O_2 instead of gaseous hydrogen (H_2), as most fuel cells today use, is that the liquid form is much easier to store at high densities. Typically, H_2 gas must be either highly compressed, or in certain cases, cooled to its liquid state at cryogenic temperatures. In contrast, liquid H_2O_2 can be stored and transported at high densities much more easily and safely. The problem is that that, until now, there has been no efficient photocatalytic method of producing liquid H_2O_2 . (There are ways to produce H_2O_2 that don't use sunlight, but they require so much energy that they are not practical for use in a method whose goal is to produce energy.) In the new study, the researchers developed a new photoelectrochemical cell, which is basically a solar cell that produces H_2O_2 . When sunlight illuminates the photocatalyst, the photocatalyst absorbs photons and uses the energy to initiate chemical reactions (seawater oxidation and the reduction of O_2) in a way that ultimately produces H_2O_2 .

After illuminating the cell for 24 hours, the concentration of H_2O_2 in the seawater reached about 48 mM, which greatly exceeds previous reported values of about 2 mM in pure water. Investigating the reason for this big difference, the researchers found that the negatively charged chlorine in seawater is mainly responsible for enhancing the photocatalytic activity and yielding the higher concentration. Overall, the system has a total solar-to-electricity efficiency of 0.28%. (The photocatalytic production of H_2O_2 from seawater has an efficiency of 0.55%, and the fuel cell has an efficiency of 50%). Although the total efficiency compares favorably to that of some other solar-to-electricity sources, such as switchgrass (0.2%), it is still much lower than the efficiency of conventional solar cells. In the future, we plan to work on developing a method for the low-cost, large-scale production of H_2O_2 from seawater. This may replace the current high-cost production of H_2O_2 from H_2 (from mainly natural gas) and O_2 .

 ASSORTED LEARNING ELEVATORS

SHORTCUT METHODS



Here, we are introducing some important shortcut methods on Atomic Structure to save your precious time in tedious calculations based problem asked in various engineering entrance exams. Use these shortcuts, to practice questions and be acquainted with it.

There are many types of problems asked in engineering as well as in medical entrance exams from the topic "Atomic Structure". Some important subtopics and tricks to solve problems related to these topics are given below:

(I) Photoelectric Effect

Type I If energy of photon (E_{photon}) and work function (W) are given, kinetic energy (KE) is asked to find out, use the following equation.

$$\begin{aligned} E_{\text{photon}} &= W + \text{KE} \\ \Rightarrow \text{KE} &= E_{\text{photon}} - W \quad \dots(i) \end{aligned}$$

Type II If frequency (ν) of photon and threshold frequency of electron (ν_0) are given and velocity of electron is asked to find out.

Step 1 Write down the formulae of E_{photon} , W and KE

$$E_{\text{photon}} = h\nu; W = h\nu_0; \text{KE} = \frac{1}{2}mv^2$$

Step 2 Put these terms in Eq. (i)

$$\frac{1}{2}mv^2 = h\nu - h\nu_0$$

Step 3 Find the value of v

$$v = \sqrt{\frac{2(h\nu - h\nu_0)}{m}}$$

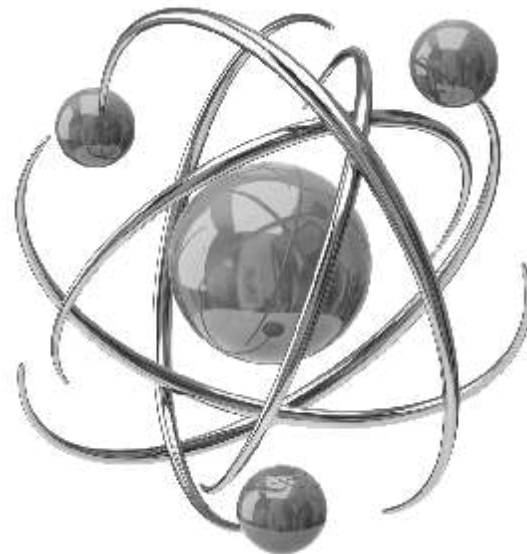
Type III If threshold wavelength (λ_0) and velocity (v) of electron are given, wavelength of photon (λ) is asked, put the terms

$$E_{\text{photon}}; \text{KE and } W \text{ in Eq. (i)}$$

$$E_{\text{photon}} = \frac{hc}{\lambda}; W = \frac{hc}{\lambda_0}; \text{KE} = \frac{1}{2}mv^2$$

$$\text{From Eq. (i), } \frac{1}{2}mv^2 = \frac{hc}{\lambda} - \frac{hc}{\lambda_0}$$

$$\frac{hc}{\lambda} = \frac{hc}{\lambda_0} + \frac{1}{2}mv^2 \quad \text{or} \quad \frac{1}{\lambda} = \frac{1}{hc} \left(\frac{hc}{\lambda_0} + \frac{1}{2}mv^2 \right)$$



Type IV If energy of photon (E_{photon}) and energy required to stop the ejection (in eV_0) are given, work function is asked to find out, in that case, use the following relation,

$$E_{\text{photon}} = W + \text{KE}$$

$$E_{\text{photon}} = W + eV_0$$

where, V_0 = stopping potential

e = electronic charge

$$\text{or } W = E_{\text{photon}} - eV_0$$

PRACTICE PROBLEMS

- The light of wavelength 400×10^{-9} m strikes a metal surface with work function of 2.13 eV. Find the kinetic energy of the most energetic photoelectron.
[Ans. 1.56×10^{-19} J]
- The energy required to stop the ejection of electron from copper plate is 0.24 eV. Calculate the work function when radiation of $\lambda = 253.7$ nm strikes the plate.
[Ans. 4.65 eV]
[Hint $1\text{eV} = 1.602 \times 10^{-19}$ J]

(II) Rydberg's Equation

The following types of problems are asked related to Rydberg's equation.

Type I To find wavelength related to different series of hydrogen spectrum.

Step 1 Find the value of n_1 and n_2 (where, $n_1 > n_2$).

Step 2 Apply Rydberg's equation, $\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$

Type II To find energy emitted/absorbed during a transition from n_1 to n_2 .

Step 1 Apply Rydberg's equation and find λ .

Step 2 Find the value of E from the formula, $E = h\nu = \frac{hc}{\lambda}$

Type III To find ionisation energy. As ionisation energy is the energy required to remove an electron completely from ground state, hence

$$IE = E_{\infty} - E_{\text{ground}} = 0 - (-13.6 \text{ eV}) = 13.6 \text{ eV atom}^{-1}$$

$$\text{For H-like species, } IE = \frac{Z^2}{n^2} \times 13.6 \text{ eV}$$

Type IV If it is asked to find wavelength related to H_{α} , H_{β} and H_{γ} line in Balmer series, put $n_1 = 2$ and $n_2 = 3$ for H_{α} line, put $n_1 = 2$ and $n_2 = 4$ for H_{β} line and for H_{γ} line, put $n_1 = 2$ and $n_2 = 5$ in Rydberg's equation.

PRACTICE PROBLEMS

- Calculate the wavelength of the first line in the Balmer series of hydrogen spectrum. [Ans. 656.5 nm]
- Calculate the shortest wavelength in hydrogen spectrum of Lyman series when $R_{\text{H}} = 109,677 \text{ cm}^{-1}$ [Ans. 911.7 Å]

[Hint For shortest Lyman series, energy difference between two levels showing transition, should be maximum, i.e. $n_2 = \infty$]

- The wavelength of the first line in the Balmer series is 656 nm. Calculate the wavelength of the second line and the limiting line in the Balmer series. [Ans. 485.9 nm, 3647 Å]

(III) Bohr's Model

Based on Bohr's theory for hydrogen atom and its applications on hydrogen like species, following type of problems are asked:

Type I When energy difference is given for two states and asked to find out wavelength of electron transition, apply the following relation,

$$\Delta E = \frac{hc}{\lambda}$$

where, ΔE = energy difference, h = Planck's constant, c = velocity of light, λ = wavelength of transition.

Type II When values of quantum numbers (n_i and n_f) of two energy states are given for hydrogen atom and asked to find out wavelength or frequency of electron transition, apply the following relations,

$$E_{n_i} = -\frac{13.6}{n_i^2} \text{ eV}, E_{n_f} = -\frac{13.6}{n_f^2} \text{ eV}$$

$$\Delta E = E_{n_f} - E_{n_i} = h\nu = \frac{hc}{\lambda}$$

where, ν = frequency of transition

Type III When values of quantum numbers (n_i and n_f) of two energy states are given for hydrogen like species and asked to find out wavelength or frequency of electron transition, apply the following relations,

$$E_{n_i} = -\frac{13.6Z^2}{n_i^2} \text{ eV}$$

$$E_{n_f} = -\frac{13.6Z^2}{n_f^2} \text{ eV}$$

$$\Delta E = E_{n_f} - E_{n_i} = h\nu = \frac{hc}{\lambda}$$

where, Z = atomic number of hydrogen like species

Type IV When values of quantum numbers (n_i and n_f) of two energy states are given for hydrogen or hydrogen like species and asked to find out wave number, apply the following relations,

$$\frac{1}{\lambda} = \bar{\nu} = 1.09677 \times 10^7 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{ m}^{-1} \quad [\text{for hydrogen atom}]$$

$$\frac{1}{\lambda} = \bar{\nu} = 1.09677 \times 10^7 Z^2 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{ m}^{-1}$$

[for hydrogen like species]

Here, $\bar{\nu}$ = wave number, $1.09677 \times 10^7 = R_{\text{H}} = \text{Rydberg's constant}$.

Type V When atomic number of two species are given and asked to find potential energy, apply the following formula,

$$PE = -\frac{Z_1 Z_2 e^2}{(4\pi\epsilon_0)r}$$

where, Z_1 and Z_2 are atomic numbers of two species

e = charge on electron

ϵ_0 = Permittivity of vacuum

Type VI When atomic number of species is given and asked to find out velocity of electron in n^{th} orbit, apply the following formula,

$$u_n = \sqrt{\frac{Ze^2}{mr_n}}$$

where, r_n = distance of electron from nucleus

$$r_n = r_1 \times n^2$$

PRACTICE PROBLEMS

- Determine the time period of revolution of an electron in the second Bohr orbit in hydrogen atom. [Ans. $1.22 \times 10^{-15} \text{ s}$]
- Calculate the velocity of an electron placed in 3rd orbit of H-atom. Also calculate the number of revolution/second around the nucleus. [Ans. $7.29 \times 10^7 \text{ cm s}^{-1}$, $2.44 \times 10^{14} \text{ s}^{-1}$]
- Find out the energy of H-atom in the first excited state. The value of permittivity factor $4\pi\epsilon_0 = 1.11264 \times 10^{-10} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$. [Ans. $5.443 \times 10^{-19} \text{ J}$]

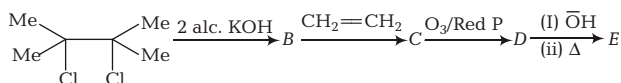
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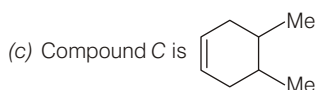
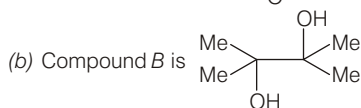
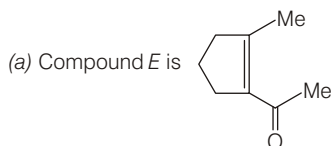
To boost up your ranks in JEE Main and Advanced

- 2.5 g of a monobasic acid when dissolved in 100 g of water elevates the boiling point of the solution by 0.15°C . If 2.5 g of the acid requires 20.40 milliequivalents of NaOH for the complete neutralisation, the degree of dissociation of the acid is (K_b of water is $0.512 \text{ K mol}^{-1}\text{kg}$)
(a) 0.367 (b) 0.436 (c) 0.764 (d) 0.257
- 2.5 mL of $\frac{2}{5} \text{ M}$ weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with $\frac{15}{2} \text{ M}$ HCl in water at 25°C .
The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C)
(a) $3.7 \times 10^{-13} \text{ M}$ (b) $3.7 \times 10^{-7} \text{ M}$
(c) $3.7 \times 10^{-2} \text{ M}$ (d) $2.7 \times 10^{-2} \text{ M}$

- Consider the following reaction sequence.



Choose the correct option.



(d) All of the above

- The gas phase decomposition of dimethyl ether follows first order kinetics,



The reaction is carried out in a constant volume container at 500°C and has half-life of 14.5 min. Initially, only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure of the system after 12 min? (Assume ideal gas behaviour)

- (a) 0.175 atm (b) 0.750 atm (c) 1.000 atm (d) 1.25 atm
- A solution of 0.04 M solution of acetic acid at 25°C has $K_a = 1.8 \times 10^{-5}$ and $\Lambda_m^\circ(\text{CH}_3\text{COOH}) = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$. What is the resistance of the cell, if its cell constant is 0.206 cm^{-1} ?
(a) 622.36 Ω (b) 589.45 Ω
(c) 736.22 Ω (d) 427.66 Ω

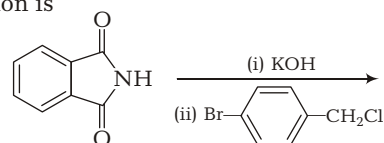
- When a certain metal was irradiated with light of frequency $3.2 \times 10^{16} \text{ Hz}$, the photoelectrons emitted had twice the kinetic energy as did photoelectrons emitted when the same metal was irradiated with light of frequency $2.0 \times 10^{16} \text{ Hz}$. Calculate ν_0 for the metals.

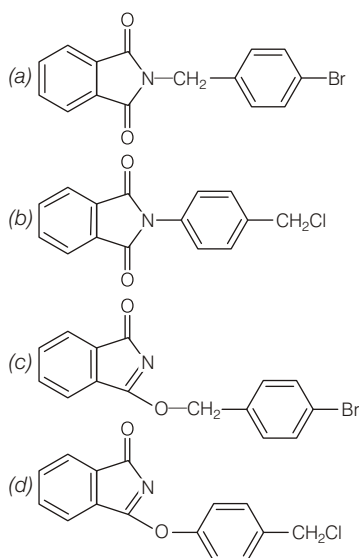
(a) $8 \times 10^{14} \text{ Hz}$ (b) $8 \times 10^{15} \text{ Hz}$ (c) $8 \times 10^{13} \text{ Hz}$ (d) $8 \times 10^{16} \text{ Hz}$

- A hydrated metallic salt A is light green in colour. On careful heating, it gives a white anhydrous residue B which is soluble in water and its aqueous solution reacts with NO to give a dark brown compound C. B on heating, produces a mixture of products. How many products are formed?

(a) 1 (b) 2
(c) 3 (d) 4

- The major product obtained in the following reaction is





9. Caesium bromide has CsCl type arrangement. If the density of caesium bromide is 4.44 g cm^{-3} , the ratio of the radius of Cs^+ and Br^- is (molecular mass of $\text{CsBr} = 213 \text{ g mol}^{-1}$)

(a) 1.574 : 2.15 (b) 1.762 : 2.15
(c) 1.51 : 2.06 (d) 1.76 : 4.21

10. Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of KMnO_4 (20 mL) acidified with dilute H_2SO_4 . The same volume of the KMnO_4 solution is just decolourised by 10 mL of MnSO_4 in neutral medium simultaneously forming dark brown precipitate of hydrated MnO_2 . The brown precipitate is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of H_2SO_4 . Calculate molarity of H_2O_2 .

(a) 0.10 M (b) 0.15 M
(c) 0.01 M (d) 0.25 M

Answers with Explanation

1. (b) Milliequivalents of NaOH requires for neutralisation = 20.40

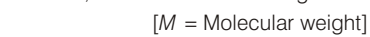
At neutralisation point,

Milliequivalent of HA = Milliequivalent of NaOH

$$\frac{2.5}{E} \times 1000 = 20.40 \Rightarrow E = \frac{2500}{20.40} = 122.5 \text{ g mol}^{-1}$$

Where, E = Equivalent weight

Since, HA is a monobasic acid, hence $E = M = 122.5 \text{ g mol}^{-1}$



Before dissociation 1 0 0
After dissociation 1 - α α α

For the above dissociation reaction, the van't Hoff factor,

$$i = (1 - \alpha) + \alpha + \alpha = 1 + \alpha$$

$$\text{Now, molality } (m) = \frac{W_{\text{solute}} \times 1000}{M_{\text{solute}} \times W_{\text{solvent}}} = \frac{2.5 \times 1000}{122.5 \times 100} = 0.204 \text{ molal}$$

Elevation in boiling point

$$\Delta T_b = i \times K_b \times m \Rightarrow 0.15 = (1 + \alpha) \times 0.512 \times 0.204$$

$$\Rightarrow (1 + \alpha) = 1.436 \Rightarrow \alpha = 0.436 \text{ or } = 43.6\%$$

2. (d) Millimoles of base = $2.5 \times \frac{2}{5} = 1$

Millimoles of acid required to reach the end point = 1

Volume of acid required to reach the end point = $\frac{15}{2}$ mL

Total volume at the end point = $\frac{15}{2} + 2.5 = 10$ mL

Molarity of salt at the end point = $\frac{1}{10} = 0.10$

Equation of hydrolysis is,



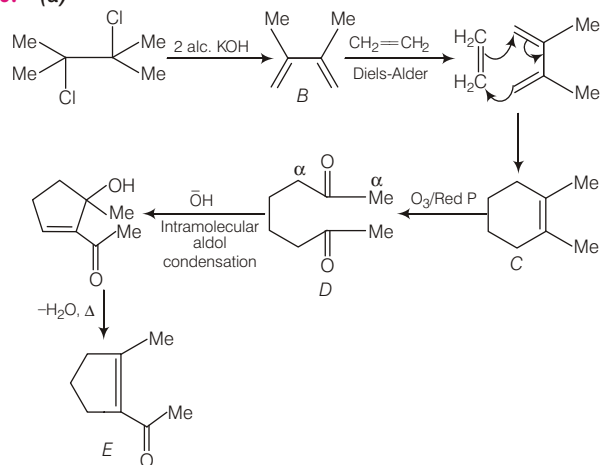
$$K_h = \frac{K_w}{K_b} \Rightarrow 10^{-2} = \frac{C\alpha^2}{1 - \alpha} \quad \text{or} \quad 10^{-2} = \frac{0.1\alpha^2}{1 - \alpha}$$

$$\text{or} \quad 10\alpha^2 + \alpha - 1 = 0$$

$$\text{or} \quad \alpha = \frac{-1 + \sqrt{1 + 40}}{20} = 0.27$$

$$\text{Now } [\text{H}^+] = C\alpha = 0.1 \times 0.27 = 0.027 \text{ M} = 2.7 \times 10^{-2} \text{ M}$$

3. (a)



4. (b) $\text{CH}_3\text{OCH}_3(\text{g}) \longrightarrow \text{CH}_4(\text{g}) + \text{H}_2(\text{g}) + \text{CO}(\text{g})$

Initial pressure 0.40 atm 0 0 0

Final pressure (0.40 - p) atm p p p
after 12 min

For a first order reaction,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a - x} \quad \dots \text{(i)}$$

 BRAIN TEASERS

For ideal gas behaviour,

Number of moles \propto pressure (at constant V and T)

$$a \propto 0.40, \quad (a - x) \propto (0.40 - p)$$

$$k = \frac{0.693}{t_{1/2}} \quad \dots \text{(ii)}$$

$$\text{or } \frac{0.693}{14.5} = \frac{2.303}{12} \log_{10} \frac{0.40}{(0.40 - p)} \quad [\text{from Eqs. (i) and (ii)}]$$

$$p = 0.175 \text{ atm}$$

\therefore Pressure of ether decomposed = 0.175 atm

Total pressure = $0.40 - p + p + p + p = 0.40 + 2p$

$$= 0.40 + 2(0.175) = 0.75 \text{ atm}$$

5. (a) Given, molarity of acetic acid solution = 0.04 M

$$K_a = 1.8 \times 10^{-5}$$

$$\Lambda_m^{\circ}(\text{AcOH}) = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$$

Cell constant = 0.206 cm^{-1}

By Ostwald's dilution law,

$$x = \sqrt{\frac{K_a}{C}}; \quad [x = \text{degree of dissociation}]$$

$$\text{and } x = \frac{\Lambda_m}{\Lambda_m^{\circ}} \Rightarrow \frac{\Lambda_m}{\Lambda_m^{\circ}} = \sqrt{\frac{K_a}{C}}$$

$$\text{or } \Lambda_m = \Lambda_m^{\circ} \sqrt{\frac{K_a}{C}} = 390.5 \sqrt{\frac{1.8 \times 10^{-5}}{0.04}} = 8.28 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\text{Molar conductivity, } \Lambda_m = \frac{\kappa \times 1000}{C}$$

$$\Rightarrow \kappa = \frac{C \times \Lambda_m}{1000} = \frac{0.04 \times 8.28}{1000}$$

\therefore Specific conductivity, $\kappa = \text{Cell constant} \times \frac{1}{\text{Resistance}}$

$$\text{or Resistance} = \frac{0.206}{3.31 \times 10^{-4}} = 622.36 \Omega$$

6. (b) According to photoelectric effect equation,

$$\text{Kinetic energy (KE)} = h\nu - h\nu_0 \quad \text{or } (v - v_0) = \frac{\text{KE}}{h}$$

Given, $v_1 = 3.2 \times 10^{16}$ Hz, $v_2 = 2.0 \times 10^{16}$ Hz

and $(\text{KE})_1 = 2(\text{KE})_2$

$$\therefore v_2 - v_0 = \frac{(\text{KE})_2}{h} \quad \dots \text{(i)} \quad \text{and } v_1 - v_0 = \frac{(\text{KE})_1}{h} \quad \dots \text{(ii)}$$

On dividing Eq. (ii) by Eq. (i), we get

$$\frac{v_1 - v_0}{v_2 - v_0} = \frac{(\text{KE})_1}{(\text{KE})_2} = \frac{2(\text{KE})_2}{(\text{KE})_2} = 2$$

$$\text{or } v_1 - v_0 = 2v_2 - 2v_0$$

$$\text{or } v_1 - 2v_2 = -v_0$$

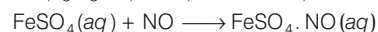
$$\Rightarrow v_0 = 2v_2 - v_1$$

$$v_0 = 2(2 \times 10^{16}) - (3.2 \times 10^{16})$$

$$= 8 \times 10^{15} \text{ Hz}$$

7. (c) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow{\Delta} \text{FeSO}_4$

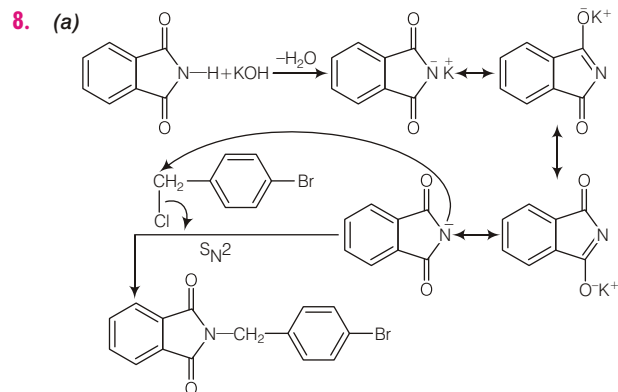
(Light green) (Soluble in water)



C



Three products are obtained.



9. (a) Since, CsBr has CsCl type arrangement hence, CsBr will have body-centred cubic arrangement with Br^- ions occupying all the corners of unit cell and Cs^+ occupying at the body-centre of unit cell. Hence, Z_{eff} for CsBr = 1

Now, density of unit cell can be calculated as

$$\rho = \frac{Z_{\text{eff}} \times M_{\text{CsBr}}}{a^3 \times N_A} \Rightarrow 4.44 = \frac{1 \times 213}{a^3 \times 6.023 \times 10^{23}}$$

$$\Rightarrow a = \left(\frac{213}{4.44 \times 6.023 \times 10^{23}} \right)^{1/3}$$

$$= 4.30 \times 10^{-8} \text{ cm} = 4.30 \times 10^{-10} \text{ m} = 4.30 \text{ \AA}$$

$$\text{For bcc arrangement, } r^+ + r^- = \frac{a\sqrt{3}}{2} = \frac{4.30\sqrt{3}}{2} = 3.724 \text{ \AA}$$

Also for bcc arrangement, $2r^- = a$

$$\text{or } r^- = \frac{a}{2} = 2.15 \text{ \AA} \quad \text{or } r^+ = (3.724 - 2.15) \text{ \AA} = 1.574 \text{ \AA}$$

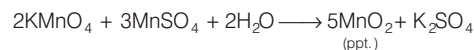
\therefore Radius ratio, $\text{Cs}^+ : \text{Br}^- = 1.574 : 2.15$

10. (a) $\text{MnO}_2 + \text{Na}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{MnSO}_4 + 2\text{CO}_2$
ppt. + $\text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$... (i)

Milliequivalent of $\text{Na}_2\text{C}_2\text{O}_4 = \text{Volume (mL)} \times \text{normality}$

$$= \text{Volume (mL)} \times n\text{-factor} \times \text{molarity} = 10 \times 2 \times 0.2 = 4$$

Reaction of KMnO_4 solution with MnSO_4 in neutral medium is given as



(ppt.)

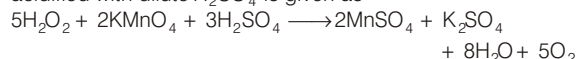
+ $2\text{H}_2\text{SO}_4$... (ii)

From Eq. (i) and Eq. (ii), we may conclude that Milliequivalents of MnO_2 formed = Milliequivalents of oxalate = 4

Milliequivalent of MnO_2 formed

$$= \text{Milliequivalent of } \text{KMnO}_4 = 4$$

Reaction of H_2O_2 (20 mL) with KMnO_4 (20mL) solution acidified with dilute H_2SO_4 is given as



\therefore Milliequivalent of KMnO_4 in 20 mL = Milliequivalent of H_2O_2 in 20 mL

$$4 = \text{Volume of } \text{H}_2\text{O}_2 \text{ (mL)} \times \text{Normality of } \text{H}_2\text{O}_2$$

$$4 = 20 \times \text{Normality of } \text{H}_2\text{O}_2$$

$$\text{Normality of } \text{H}_2\text{O}_2 = \frac{4}{20} = 0.2 \text{ N}$$

$$\text{or Molarity of } \text{H}_2\text{O}_2 = \frac{\text{Normality}}{n\text{-factor}} = \frac{0.2}{2} = 0.10 \text{ M}$$

 MASTER THE NCERT

SOME BASIC CONCEPT OF CHEMISTRY



This section of magazine is aimed to increase the connectivity between reader and NCERT Textbook. Readers are advised to solve these questions with the help of references of NCERT given at the end of this section.

- Consider the following statements
 - ...A... deals with the composition, structure and properties of matter.
 - Chemistry is called as the science of ...B... .
 - The area of applications of the chemical principles is ...C... .
 - Science can be viewed as a continuing ...D... . to systematise knowledge for describing and understanding nature.

Here, A, B, C and D refer to

	A	B	C	D
(a) Chemistry	atoms and molecules	operation of a computer and weather pattern	human effort	
(b) Biology	atoms	function of brain	non-human effort	
(c) Physics	electrons	weather pattern	human effort	
(d) Chemistry	molecules and atoms	operation of a computer	non-human effort	

- Consider the following statements.
 - Chemistry is the branch of science that studies the composition, properties and interaction of matter.
 - Chemistry plays a central role in science and is often intertwined with other branches of science like Physics, Biology, Geology etc.
 - Chemistry plays an important role in daily life.
 Select the correct statement(s) and mark the correct option.
 - Only I
 - II and III
 - I, II and III
 - I and II

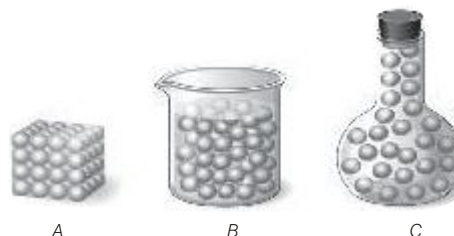
- Match the following Column I with Column II and choose the correct code that are given below.

Column I (Compound)	Column II (Use)
A. Cis-platin	I. Helping AIDS victims
B. Azidothymidine	II. Saving drugs for cancer therapy
C. Taxol	III. Environmentally hazardous refrigerants
D. Chlorofluorocarbons	

Codes

	A	B	C	D		A	B	C	D
(a)	II	I	III	III	(b)	II	I	I	III
(c)	II	II	I	III	(d)	I	II	I	III

- A developing country like India needs talented and creative chemists for accepting intellectual challenges like
 - understanding of biochemical process
 - use of enzymes for large scale production of chemicals
 - synthesis of new exotic materials
 - All of the above
- Observe the following figures carefully and label A, B and C for the arrangement of particles in solid, liquid and gaseous state.



Identify which of the following choices is correct?

- A → gas, B → solid, C → liquid
- A → solid, B → liquid, C → gas
- A → liquid, B → solid, C → gas
- A → gas, B → liquid, C → solid

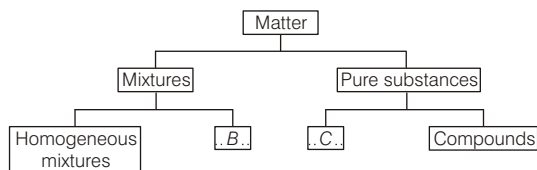

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6. Consider the following statements.
- Solids have definite volume and definite shape.
 - Liquids have definite volume and definite shape however, they take the shape of the container in which they are placed.
 - Gases neither have definite volume nor definite shape and they completely occupy the shape of the container in which they are placed.

Identify whether the above statements are true (T) or false (F) and mark the correct option that are given below.




- | | | | | | |
|-------|----|-----|-------|----|-----|
| I | II | III | I | II | III |
| (a) T | F | F | (b) F | F | T |
| (c) T | T | T | (d) T | F | T |

7. At the ...A..., matter can be classified as mixtures or pure substances. These can be further subdivided as shown below.



Observe the above flow chart carefully and label the fill ups appropriately. Here, A, B and C refer to

- A → microscopic level, B → heterogeneous mixtures, C → elements
 - A → macroscopic level, B → heterogeneous mixtures, C → elements
 - A → microscopic level, B → elements, C → heterogeneous mixtures
 - A → macroscopic level, B → elements, C → heterogeneous mixtures
8. Match the items given in Column I with the items given in Column II and choose the correct code that are given below.

Column I	Column II
A. 	I. Atom
B. 	II. Compound
C. 	III. Molecule

Codes

- | | | | | | |
|---------|-----|----|---------|----|-----|
| A | B | C | A | B | C |
| (a) III | I | II | (b) I | II | III |
| (c) II | III | I | (d) III | II | I |

9. Consider the following statements.
- Mixture may contain the components in any ratio and their composition is variable.
 - Pure substances have fixed composition.

- The constituents of pure substances cannot be separated by simple physical methods.
- Copper, glucose, silver, gold, water are the examples of pure substances.

Select the correct statement(s) and mark the correct option.

- (a) Only I (b) I and II (c) III and IV (d) I, II, III and IV

10. Match the Column I, Column II and Column III and choose the correct option from the codes given below.

Column I (Multiple)	Column II (Prefix)	Column III (Symbol)
A. 10^{-15}	p. Kilo	1. m
B. 10^{-3}	q. Yotta	2. f
C. 10^3	r. Milli	3. k
D. 10^{24}	s. Fento	4. y

Codes

- | | | | |
|------------|--------|--------|--------|
| A | B | C | D |
| (a) (s, 2) | (r, 1) | (p, 3) | (q, 4) |
| (b) (q, 4) | (s, 3) | (r, 3) | (p, 1) |
| (c) (p, 1) | (r, 3) | (q, 3) | (s, 4) |
| (d) (s, 2) | (p, 3) | (r, 1) | (q, 4) |

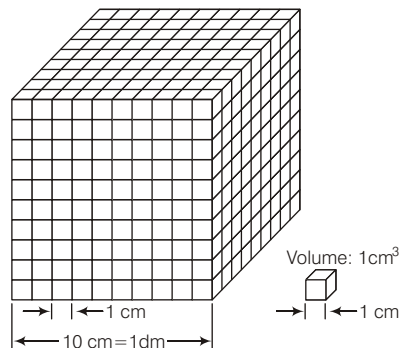
11. Match the Column I with the Column II and choose the correct option from the codes given below.

Column I (Basic physical quantity)	Column II (Symbol for quantity)
A. Amount of substance	I. I
B. Temperature	II. T
C. Mass	III. m
D. Luminous intensity	IV. I_v
E. Electric current	V. m

Codes

- | | | | | | | | | | |
|---------|-----|----|----|----|-------|-----|----|----|-----|
| A | B | C | D | E | A | B | C | D | E |
| (a) III | II | V | IV | I | (b) I | III | II | IV | V |
| (c) I | III | II | V | IV | (d) V | IV | I | II | III |

12. Calculate the volume of the given cube in mL.



Choose the correct option.

- (a) 10 mL (b) 100 mL
(c) 1000 mL (d) None of these

13. Consider the following statements.
- ...A... of a substance is the amount of matter present in it while ...B... is the force exerted by gravity on an object.
 - It is inserted to note that temperature below 0°C (i.e. negative values) are possible in ...C... but in ...D..., negative temperature is not possible.
 - The SI unit of volume is ...E... and the metric unit for volume is ...F....

Here A, B, C, D, E and F refer to

	A	B	C	D	E	F
(a) Mass	Weight	Celsius scale	Kelvin scale	m^3	L	
(b) Weight	Mass	Celsius scale	Fahrenheit scale	L	m^3	
(c) Mole	Pressure	Kelvin scale	Celsius scale	cm^3	m^3	
(d) Luminous intensity	Weight	Fahrenheit scale	Kelvin scale	mL	m^3	

14. Match the Column I with Column II in terms of correct number of significant figures and mark the correct code that are given below.

Column I	Column II
A. $(9.8 \times 10^{-2}) \times (2.5 \times 10)$	I. 2.450×10^{-7}
B. $\frac{2.7 \times 10^{-3}}{5.5 \times 10^4}$	II. 24.50×10^{-8}
C. $(6.65 \times 10^4) + (8.95 \times 10^3)$	III. 0.4909×10^{-7}
	IV. 4.909×10^{-9}
	V. 7.545×10^4
	VI. 754.5×10^2

Codes

A	B	C	A	B	C
(a) I	III	V	(b) II	IV	VI
(c) I	IV	V	(d) II	III	V

15. How many significant figures are present in 8.256×10^{-3} ?
- 7
 - 4
 - 3
 - 10

16. Let the true value for a result is 2.00 g. Three students A, B and C take two measurements and report the result. Data to illustrate precision and accuracy is given below.

Student	Measurements/g		Average (g)
	1	2	
Student A	1.95	1.93	1.940
Student B	1.94	2.05	1.995
Student C	2.01	1.99	2.000

Which of the following students got the values which are both precise and accurate?

- Student A
- Student B
- Student C
- None of these

17. Consider the following statements regarding the significant figures and their calculations.

- The result of an addition or subtraction is reported to the same number of decimal places as present in number with least decimal places.
- Result of multiplication or division should have same number of significant figures as present in most precise figure.
- The result of multiplication or division should be rounded off to same number of significant figures as present in least precise figure.
- The non-significant figures in the measurements are rounded off.

Select the correct statement(s) and mark the correct option that are given below.

- Only I
- I and III
- I, III and IV
- All of these

18. Which law states that matter can neither be created nor destroyed?

- Law of definite proportions
- Law of conservation of mass
- Law of multiple proportions
- Avogadro's law

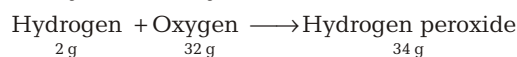
19. Consider the following statements.

- Gay Lussac's law was explained properly by the work of ...A... in 1811.
- In 1811, Avogadro proposed that equal volumes of gases at the same ...B... and ...C... should contain equal number of molecules.
- According to Avogadro's law, two volumes of hydrogen combine with one volume of oxygen to give two volumes of water without leaving any ...D... oxygen.

Here, A, B, C and D respectively refer to

- Dalton, density, mass, massive
- Avogadro, temperature, pressure, unreacted
- Gay Lussac, molarity, normality, residual
- Antoine Lavoisier, Avogadro's constant, Planck's constant, reacted

20. Hydrogen combines with oxygen to form two compounds namely, water and hydrogen peroxide.



Here, the masses of oxygen which combine with a fixed mass of hydrogen (2 g) bear simple ratio, i.e. ...A... .

Here, A refers to

- 2 : 1
- 1 : 2
- 3 : 4
- 4 : 3

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21. Consider the following statements.
- Matter consists of indivisible atoms.
 - All the atoms of a given element have identical properties including identical mass.
 - Compounds are formed when atoms of different elements combine in any ratio.
 - Chemical reactions involve reorganisation of atoms. These are neither created nor destroyed in a chemical reaction.

Select the correct statement(s) and mark the correct option that are given below.

- I and II
- I and IV
- III and IV
- I, II and IV

22. Carbon has the following three isotopes with relative abundances and masses (amu) shown in the following table:

Isotopes	Relative abundance (%)	Atomic mass (amu)
^{12}C	98.892	12
^{13}C	1.108	13.00335
^{14}C	2×10^{-10}	14.00317

From the above data, the average atomic mass of carbon will come out to be

- 12.000 u
- 12.011 u
- 12.015 u
- 13.000 u

23. Consider the following statements.
- ...A... is the sum of atomic masses of the elements present in a molecule.
 - The formula such as NaCl is used to calculate the ...B... instead of molecular mass as in the solid state, sodium chloride does not exist as a single entity.

Here, A and B refer to

- atomic mass, molecular mass
- molecular mass, formula mass
- molar mass, atomic mass
- formula mass, average atomic mass

24. Match the Column I with Column II and choose the correct option from the codes given below.

Column I (1 mole of entities)	Column II (N_A entities)
A. 1 mole of hydrogen atoms	I. 6.022×10^{23} molecules
B. 1 mole of water molecules	II. 6.022×10^{23} atoms
C. 1 mole of sodium chloride	III. 6.022×10^{23} formula

Codes

	A	B	C		A	B	C
(a)	II	III	I	(b)	II	I	III
(c)	I	II	III	(d)	III	II	I

25. What is the mass percentage of oxygen in ethanol?

- 35.14%
- 33.13%
- 34.73%
- 38.28%

26. Consider the following addition of significant figures given below

12.11

18.00

1.012

31.122

How the result should be reported in above addition?

- 31.12
- 31.1
- 31.122
- 31.10

27. An organic compound containing 49.3% carbon, 6.84% hydrogen and its vapour density is 73. Molecular formula of the compound is

- $\text{C}_3\text{H}_5\text{O}_2$
- $\text{C}_4\text{H}_{10}\text{O}_2$
- $\text{C}_6\text{H}_{10}\text{O}_4$
- $\text{C}_3\text{H}_{10}\text{O}_2$

28. Which of the following equations is an unbalanced equation?

- $\text{P}_4(\text{s}) + 5\text{O}_2(\text{g}) \longrightarrow \text{P}_4\text{O}_{10}(\text{s})$
- $\text{C}_4\text{H}_8(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
- $4\text{Fe}(\text{g}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{Fe}_2\text{O}_3(\text{g})$
- $2\text{Mg}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow 2\text{MgO}(\text{s})$

29. Match the following Column I with Column II and choose the correct code that are given below.

Column I (Terms)	Column II (Definition)
A. Mole fraction	I. It is defined as the number of moles of solute present in 1 kg of solvent.
B. Molarity	II. It is the ratio of number of moles of a partial component to the total number of moles of the solution.
C. Molality	III. It is defined as the number of moles of the solute in 1 L of the solution.

Codes

	A	B	C		A	B	C
(a)	II	III	I	(b)	I	II	III
(c)	I	III	II	(d)	II	I	III

30. The density of 2 M solution of NaCl is 1.35 g mL^{-1} . The molality of the solution is

- 2.79 m
- 1.622 m
- 2.68 m
- 1.33 m

Correct Answers along with NCERT Textbook Reference

- | | | | |
|--|----------------|---|-----------------|
| 1. (a) Subunit : Introduction Importance of Chemistry, | Page No. 1 | 18. (b) Subunit : Laws of Chemical Combination (Law of Conservation of Mass), | Page No. 11 |
| 2. (c) Subunit : Importance of Chemistry, | Page No. 1 | 19. (b) Subunit : Gay Lussac's Law of Gaseous Volumes; Avogadro's Law, | Page No. 12 |
| 3. (b) Subunit : Importance of Chemistry, | Page No. 2 | 20. (b) Subunit : Gay Lussac's Law of Gaseous Volumes | Page No. 12 |
| 4. (d) Subunit : Importance of Chemistry, | Page No. 2 | 21. (d) Subunit : Dalton's Atomic Theory, | Page No. 13 |
| 5. (b) Subunit : Nature of Matter, | Page No. 2 | 22. (b) Subunit : Average Atomic Mass, | Page No. 13 |
| 6. (c) Subunit : Nature of Matter, | Page No. 2 | 23. (b) Subunit : Molecular Mass; Formula Mass, | Page No. 14 |
| 7. (b) Subunit : Nature of Matter, | Page No. 3 | 24. (b) Subunit : Mole Concept and Molar Masses, | Page No. 15 |
| 8. (a) Subunit : Nature of Matter, | Page No. 3 | 25. (c) Subunit : Percentage Composition, | Page No. 15 |
| 9. (d) Subunit : Nature of Matter, | Page No. 3,4 | 26. (b) Subunit : Addition and Subtraction of Significant Figures, | Page No. 10 |
| 10. (a) Subunit : The International System of Unit (SI), | Page No. 5 | 27. (c) Subunit : Empirical Formula for Molecular Formula, | Page No. 16 |
| 11. (a) Subunit : The International System of Unit (SI), | Page No. 5 | 28. (b) Box-matter : Balancing of a Chemical Equation, | Page No. 17 |
| 12. (b) Subunit : Volume | Page No. 6 | 29. (a) Subunit : Mole Fraction; Molarity and Molality, | Page No. 20 |
| 13. (a) Subunit : Mass and Weight; Temperature | Page No. 6,7,8 | 30. (b) Subunit : Molality | Page No. 20, 21 |
| 14. (a) Subunit : Uncertainty in Measurement, | Page No. 9 | | |
| 15. (b) Subunit : Significant Figures, | Page No. 9 | | |
| 16. (c) Subunit : Significant Figures, | Page No. 9 | | |
| 17. (c) Subunit : Significant Figures, | Page No. 9,10 | | |

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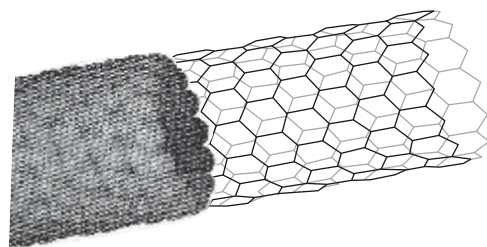
Molecular Wires

The Conductors of Tomorrow

Most of the macromolecules and self-assembled structures are insulators, or very poor electrical conductors. However, a variety of newly developed macromolecular materials have electrical conductivities that rival those of silicon-based semiconductors and even metallic conductors. The hope is that these materials will form the basis for cheaper and smaller electronic devices, including micrometre and even smaller electronic devices, including micrometre and even nanometre scale transistors, sensors, and computer chips.

Here, we examine two examples: **Carbon nanotubes**, in which carbon atoms assemble into thin cylinders that are both mechanically strong and highly conducting, and **conducting polymers**, in which extensively conjugated double bonds facilitate electron conduction along a polymer chain. **A.J. Heeger, A.J. McDiarmid, and H. Shirakawa are credited for working in the synthesis and characterisation of conducting polymers. They were also awarded with Nobel prize in 2000 for the same.**

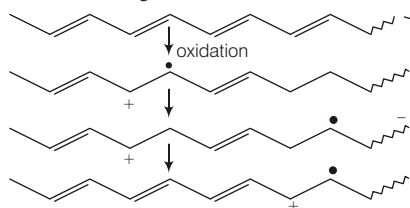
Carbon nanotubes form under some of the same conditions that lead to the formation of Fullerenes, C_{60} and C_{70} . In recent years, methods for more selective synthesis of nanotubes have been developed and they consist of different ways to condense a carbon plasma either in the presence or absence of a catalyst. The simplest structure is called a **single walled nanotube** (SWNT) and is shown in the figure below.



In an SWNT, sp^2 hybridised carbon atoms form hexagonal rings recalls of the structure of the carbon sheets found in graphite. The tubes have diameters between 1 and 2 nm and lengths of several microns. The features shown in the figure have been confirmed by direct visualisation with scanning tunnelling microscopy. A **multi-walled nanotube** (MWNT) consists of several concentric SWNTs and its diameter varies between 2 and 25 nm.

The origin of electrical conductivity in carbon nanotubes is the delocalisation of π bonds that form from unhybridised p-orbitals. Recent studies have shown a correlation between structure and conductivity in SWNTs. The above figure shows a SWNT that is a semiconductor, with conductivity intermediate between that of an insulator and of a metallic conductor. If the hexagons are rotated by 60° , the resulting SWNT has the characteristics of a metallic conductor.

The mechanism of electrical conduction in conducting polymers is more complex. One example of a conducting polymer is polyacetylene shown in the figure below. Where the delocalised π bonds suggest that electrons can move up and down through the chain. The electrical conductivity of polyacetylene increases significantly when it is partially oxidised by other strong oxidants. The product is a **polaron**, a partially localised cation radical that does not delocalise but rather travels through the chain, as shown in the figure below.



The mechanism of migration of a partially localised cation and radical, or polaron, in polyacetylene is shown above. Further oxidation of the polymer forms either **bipolarons**, a di cation that moves as a unit through the chain, or **solitons**, two separate cation radicals that move independently. Polarons and solitons contribute to the mechanism of charge conduction in polyacetylene.

Conducting polymers are slightly better electrical conductors than silicon semiconductors but are far worse than metallic conductors. They are currently used in a number of devices, such as electrons in batteries, electrolytic capacitors, and sensors. Recent studies of photon emission by conducting polymers may lead to new technology for light-emitting diodes and flat-panel displays. Like carbon nanotubes, conducting polymers show promise as molecular wires that can be incorporated into nanometre - sized electronic devices.

In a single-walled nanotube (SWNT), sp^2 -hybridised carbon atoms form hexagonal rings that grow as tubes with diameters between 1 and 2 nm and lengths of several micrometres.

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JUST SOLVE & SEND KNOWLEDGE COEFFICIENT QUIZZER (NO. 19)

1. GaAs and GaP make solid solutions that have the same crystal structure as the parent materials, with As and P randomly distributed through the crystal. $\text{GaP}_x\text{As}_{1-x}$ exists for any value of x . If we assume that the band gap varies linearly with composition between $x=0$ and $x=1$, estimate the band gap for $\text{GaP}_{0.5}\text{As}_{0.5}$.
- (a) 2.29 eV (b) 1.85 eV (c) 1.09 eV (d) 0.80 eV

2. The reactive chemicals on the tip of a "strike anywhere" match are usually P_4S_3 and an oxidising agent such as KClO_3 . When the match is struck on a rough surface, the heat generated by the friction ignites the P_4S_3 to P_4O_{10} and SO_2 . Calculate the standard enthalpy change for the combustion of P_4S_3 in air. Given, the standard enthalpies of formation,

($\text{P}_4\text{S}_3 = -154.40 \text{ kJ mol}^{-1}$), ($\text{P}_4\text{O}_{10} = -2940.1 \text{ kJ mol}^{-1}$),
($\text{SO}_2 = -296.90 \text{ kJ mol}^{-1}$)

- (a) -3676.4 kJ (b) -3000.2 kJ
(c) -3276.9 kJ (d) -3327.8 kJ

3. Consider the following statements and mark them as true or false.

I. PbMe_4 and PbEt_4 are the compounds used as antiknocking agents in gasoline.

II. The tin atoms are 9 and 8 coordinated in SnCl_2 and SnBr_2 , respectively.

III. Ammonium nitrate volatilises reversibly at higher temperature.

IV. Arsenic trioxide dissolves in aqueous bases to give arsenite ions such as $[\text{AsO}(\text{OH})_2]^{2-}$, $[\text{AsO}_2(\text{OH})]^-$ and $[\text{AsO}_3]^{3-}$.

- | | I | II | III | IV |
|-----|-------|-------|-------|-------|
| (a) | True | True | False | False |
| (b) | False | True | False | True |
| (c) | False | False | True | True |
| (d) | True | False | True | False |

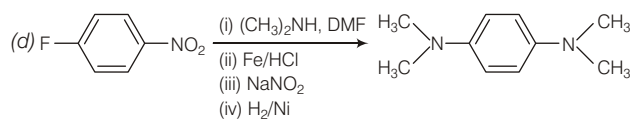
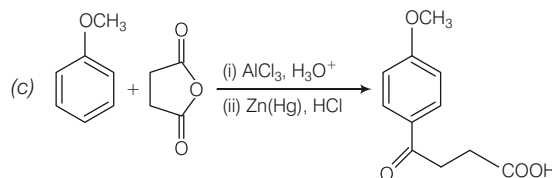
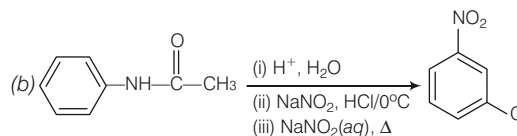
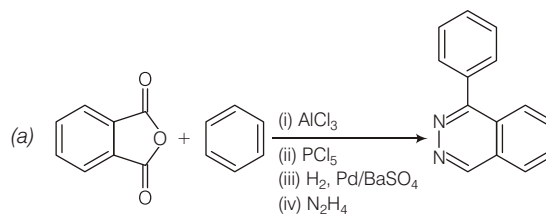
4. Match the following columns.

Column I (Ion)	Column II (Stability)
A. VO_2^+	p. Disproportionates only in strong acid
B. NpO_2^+	q. Stable in 15 M NH_4F
C. Am^{4+}	r. Stable only for 1 h at 25°C
D. Cm^{4+}	s. Stability is greatest at pH 2 to 4

Codes

- | | A | B | C | D | | A | B | C | D |
|-----|---|---|---|---|-----|---|---|---|---|
| (a) | s | r | p | q | (b) | p | s | r | q |
| (c) | s | p | q | r | (d) | p | q | s | r |

5. Choose the correct reaction from the following reactions.



 QUIZZER

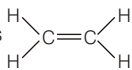
6. Nickel carbonyl, $\text{Ni}(\text{CO})_4$, can be made by the reaction of finely divided nickel metal with gaseous CO at room temperature. This is the basis for purifying nickel on an industrial scale. If you have CO in a 1.50 L flask at a pressure of 418 mm Hg at 25.0°C , what is the maximum mass in grams of $\text{Ni}(\text{CO})_4$ that can be made?

- (a) 1.79 g (b) 2.23 g
(c) 1.44 g (d) 3.14 g

7. A 1.685 g sample of a hydrocarbon is burned completely to form 5.287 g carbon dioxide and 2.164 g water.

Select the correct option regarding the above statement.

- (a) Empirical formula of hydrocarbon is C_2H_4
(b) The hydrocarbon is alkane

(c) The plausible Lewis structure of hydrocarbon is 

(d) All of the above

8. The experimental rate constant for the reaction of iodide ion with methyl bromide is $7.70 \times 10^{-3} \text{ L mol}^{-1}\text{s}^{-1}$ at 50°C and $4.25 \times 10^{-5} \text{ L mol}^{-1}\text{s}^{-1}$ at 0°C . Calculate the frequency factor.

- (a) $1.66 \times 10^{10} \text{ L mol}^{-1}\text{s}^{-1}$
(b) $0.66 \times 10^{10} \text{ L mol}^{-1}\text{s}^{-1}$
(c) $1.66 \times 10^8 \text{ L mol}^{-1}\text{s}^{-1}$
(d) $0.66 \times 10^8 \text{ L mol}^{-1}\text{s}^{-1}$

9. Choose the incorrect statement from the following.

- (a) For an endothermic reaction, an increase in temperature always means an increase in K_C
(b) For an exothermic reaction, an increase in temperature always means decrease in K_C
(c) Changing pressure by changing the volume shifts an equilibrium only if sum of the coefficients of gas phase reactants is same as that of sum of the coefficients of gas phase products
(d) The pressure of all substances in a gaseous equilibrium can be changed by changing the volume of container.

10. Determine the molar mass of the 1.55 g compound, dissolves in 75.0 g of cyclohexane, which has a freezing point of 6.50°C and a freezing point depression constant of $20.2^\circ\text{C kg mol}^{-1}$. The freezing point of the solution is measured as 2.70°C .

- (a) 102 g mol^{-1}
(b) 106 g mol^{-1}
(c) 108 g mol^{-1}
(d) 100 g mol^{-1}

KNOWLEDGE Coefficient

Quizzer (No. 19)

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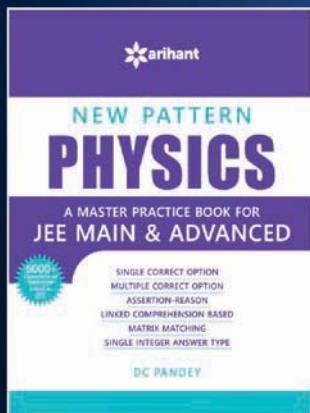


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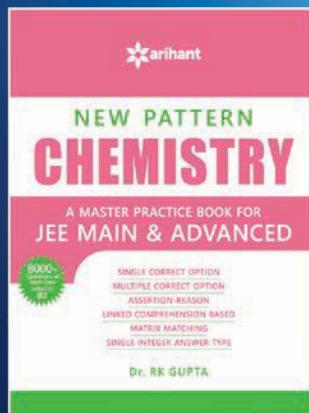
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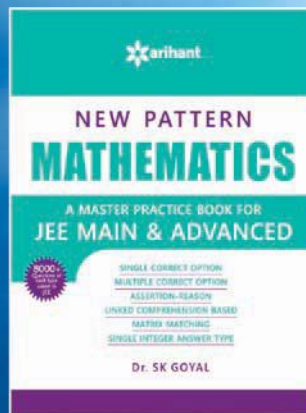
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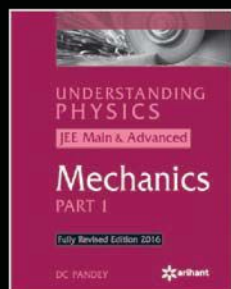
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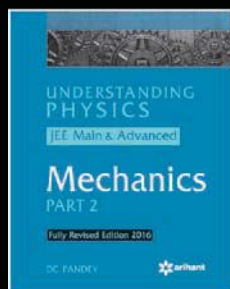
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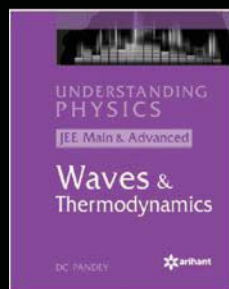
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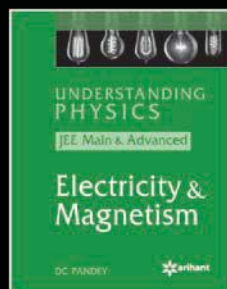
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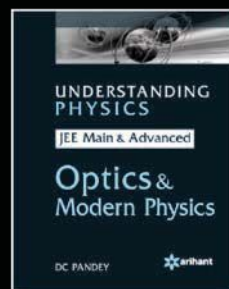
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